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LX.—*Cryptopine. Part II.*

By WILLIAM HENRY PERKIN, jun.

THE present investigation was originally undertaken with the object of clearing up some points, difficult of explanation, which had arisen during the course of the experiments described in Part I of this research.* Gradually the scope of the inquiry has widened, and many developments are included in this communication which were at first not contemplated. Broadly speaking, the basis of the new material is the series of changes represented by the conversion of cryptopine (I) into *iso*cryptopine chloride (II), and the formation of anhydrocryptopine (III) from the latter by the elimination of hydrogen chloride (833, 850).†

(I.)

(II.)

(III.)
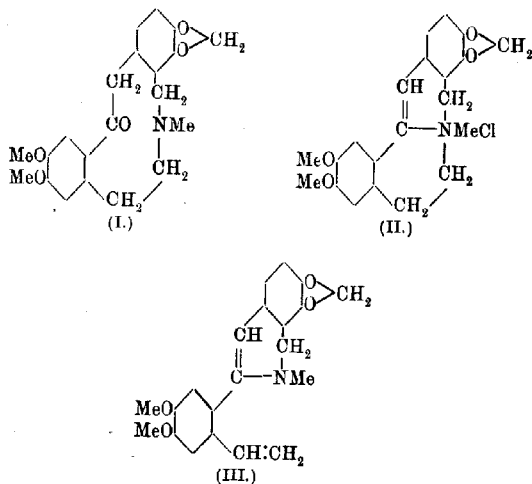
It was shown in the earlier research (852) that the properties of anhydrocryptopine are in many respects quite unusual, and one of the points most difficult of explanation is the behaviour of anhydrocryptopine methosulphate (or the corresponding methochloride) towards hydrolytic agents. Normally, the hydrolytic

* " Cryptopine and Protopine," Part I., T., 1916, **109**, 815—1028.
† The numbers in brackets—thus (833)—refer to the page in Part I.

decomposition of a methosulphate results in the formation of a new base containing a methyl group more than the original base contained. Thus cryptopine methosulphate is decomposed on hydrolysis with the formation of methylcryptopine (847).
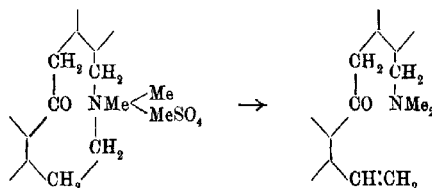
The methosulphate of anhydrocryptopine does not behave in this way (852), but is hydrolysed by methyl-alcoholic potassium hydroxide with elimination of the added methyl group and regeneration of anhydrocryptopine.
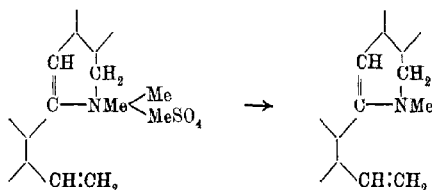
A case of this kind does not appear to have been previously recorded, and although an attempt was made (854; T., 1918, 113, 735) to find some explanation for this curious removal of a methyl group from nitrogen, it is still not clear why the N-methyldihydro-*iso*quinoline ring characteristic of anhydrocryptopine should exhibit this unusual behaviour. Recently (T., 1918, 113, 735), a welcome confirmation of the curious change just mentioned has been forthcoming, since it has been found possible to prepare from berberine the derivative—anhydromethylberberine—which corresponds exactly with anhydrocryptopine.

This substance also combines readily with methyl sulphate to yield the corresponding methosulphate, which, when boiled with methyl-alcoholic potassium hydroxide, is decomposed in exactly the same manner as anhydrocryptopine methosulphate, with regeneration of anhydromethylberberine.

Not only do alkali hydroxides cause the elimination of a N-methyl group from anhydrocryptopine methosulphate, but experiment has shown that a process of the same kind occurs even

more readily when acid reagents are employed. Thus anhydro-
cryptopine methosulphate is rapidly changed by boiling with con-
centrated hydrochloric acid, and ψ-cryptopine chloride is produced,
a decomposition which appears to be correctly represented by the
scheme (855):
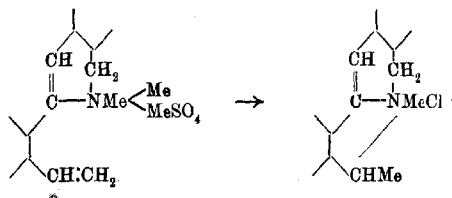
An exactly analogous change is observed when anhydromethyl-
berberine methosulphate is digested with concentrated hydrochloric
acid, ψ-methylberberinium chloride being obtained (T., 1919, **113**,
735).

In the present communication (p. 767), it is shown that concen-
trated mineral acid need not be employed in order to bring about
the elimination of the N-methyl group, since ψ-cryptopine chloride
is readily obtained when anhydrocryptopine methosulphate is
heated on the steam-bath with dilute hydrochloric acid, and
ψ-cryptopine hydrogen sulphate, $C_{21}H_{22}O_4N \cdot HSO_4$, results, in a
similar manner, from the action of dilute sulphuric acid on the
methosulphate.

The remarkable changes associated with the action of hydrolytic
agents on anhydrocryptopine methosulphate suggested the desira-
bility of making a further study of the behaviour of this substance
towards other reagents. Experiments on the oxidation of the
methosulphate did not lead to useful results, but the corresponding
methochloride is oxidised by permanganate, without elimination of
an N-methyl group and with the formation of a base, $C_{22}H_{25}O_6N$
(m. p. 188°), which appears to be produced according to the
scheme:

E E 2
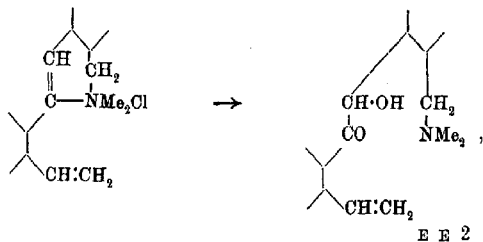
and has been named *dioxymethylisoanhydrodihydrocryptopine* (p. 738).

Of much greater interest is the behaviour of anhydrocryptopine methosulphate when subjected to the action of reducing agents, and it was the results obtained during the study of these remarkable changes which led to the extension of the subject so as to include the action of reducing agents on other derivatives of cryptopine. In order that this complex study may be made as clear and concise as possible, the subject has been divided into sections, and the sectional numbers in this summary correspond with the numbers of the sections in the experimental part.

Section I (a).   *The Reduction of Anhydrocryptopine Methosulphate by Sodium Amalgam in Alkaline Solution* (p. 740).— When sodium amalgam is added to the aqueous solution of anhydrocryptopine methosulphate, a base, $C_{22}H_{25}O_4N$—*dihydroanhydromethylcryptopine*—gradually separates, which has not been obtained crystalline, but yields a crystalline methosulphate,
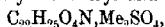
$$C_{22}H_{25}O_4N,Me_2SO_4,$$

and methiodide, $C_{22}H_{25}O_4N,MeI$. It is clear, therefore, that elimination of a methyl group had not taken place during reduction under these conditions.

On oxidation in acetone solution with permanganate, the new base yields 5 : 6-methylenedioxy-*o*-tolualdehyde (907) and 5 : 6-methylenedioxy-*o*-toluic acid (916),
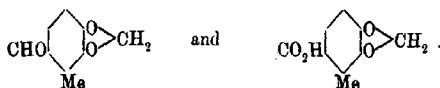
It is clear, therefore, that its formation from anhydrocryptopine methosulphate is probably represented thus:

Dihydroanhydromethylcryptopine.
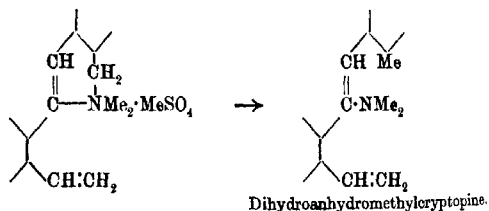
a view which has received support from the detailed investigation of the base. It has already been stated that the base yields a crystalline methosulphate, and this is readily decomposed by boil-

ing with methyl-alcoholic potassium hydroxide, with elimination of trimethylamine and formation of a new substance, $C_{20}H_{20}O_5$:

Hydroxycryptopidene.
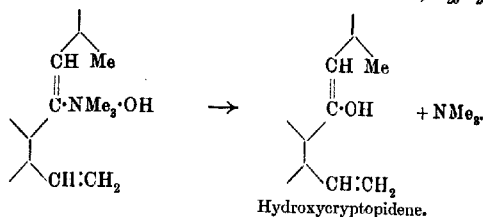
Hydroxycryptopidene * melts at 88—90°, and yields, on oxidation with permanganate, 5 : 6-methylenedioxy-o-toluic acid,

$$CH_2:O_2:C_6H_2Me\cdot CO_2H$$

(916), and 4 : 5-dimethoxy-2-vinylbenzaldehyde,

$$(MeO)_2C_6H_2(CHO)\cdot CH:CH_2$$

(904), the former containing the upper and the latter the lower portion of the molecule.
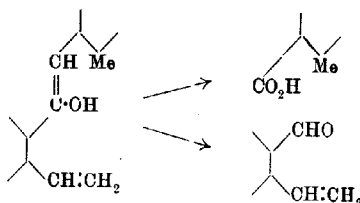
This fission clearly demonstrates the constitution of the substance, $C_{20}H_{20}O_5$, and indirectly that also of dihydroanhydromethylcryptopine.

Hydroxycryptopidene is isomeric and closely allied with *a-iso*cryptopidol (m. p. 92°; 843), which results in a similar manner from methyl*iso*anhydrodihydrocryptopine methosulphate by the elimination of trimethylamine:

a-*iso*Cryptopidol.
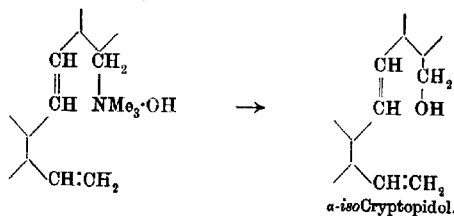
* Compare (926) for a description of the parent substance cryptopidene.

Hydroxycryptopidene does not yield an acetyl derivative, but is converted by the action of acetyl chloride into a polymeric modification, $(C_{20}H_{20}O_5)_n$, which melts at about 200°, and corresponds closely in properties and composition with the β-modification of *iso*cryptopidol (843).

Section I (b).   *The Reduction of Anhydrocryptopine Methosulphate by Sodium Amalgam in Acid Solution* (p. 743).—When anhydrocryptopine methosulphate is reduced by sodium amalgam in the presence of a large excess of hydrochloric acid, disruption of the central ring takes place in a manner similar to that described in Section I (*a*), but with the addition of four atoms of hydrogen and again without the elimination of a methyl group. The product is a base, $C_{22}H_{27}O_4N$—*tetrahydroanhydromethylcryptopine*— and its properties are in harmony with its formation, according to the scheme:
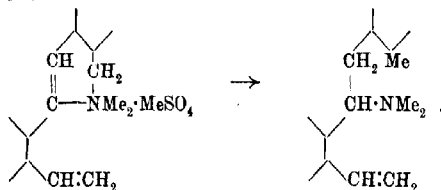
This base has not been obtained crystalline, and is isomeric with anhydrotetrahydromethylcryptopine (898), which is crystalline

Tetrahydroanhydromethyl-
cryptopine methohydroxide.

Cryptopidene.

Anhydrotetrahydromethyl-
cryptopine methohydroxide.
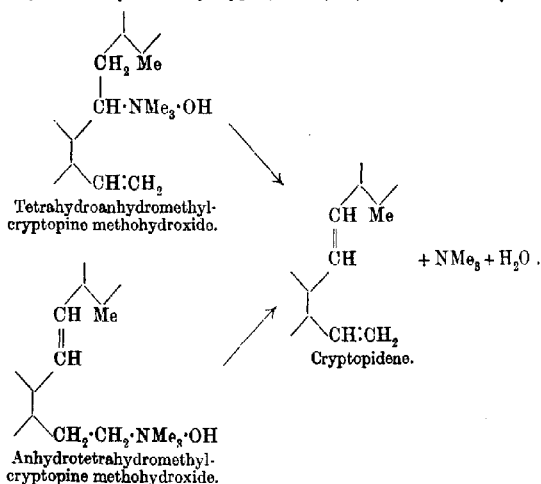
and melts at 107°.   The close relationship between these bases is well brought out when their formulæ are written side by side and by the fact that the methosulphates of both are decomposed by boiling with methyl-alcoholic potassium hydroxide, with elimination of trimethylamine and separation of cryptopidene (m. p. 123°; see above).

A further stage in the reduction of the cryptopine molecule has been achieved by the preparation of *dihydrocryptopidene*, $C_{20}H_{22}O_4$ (m. p. 128°), and the reduction of cryptopidene to *tetrahydrocryptopidene*, $C_{20}H_{24}O_4$:
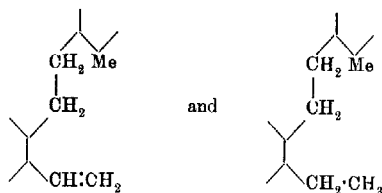
The first of these is obtained by a process described on p. 762, and the latter is produced when cryptopidene is reduced in boiling alcoholic solution with sodium.   It is one of the most beautiful substances in the cryptopine series, melts at 78°, and crystallises in stout, colourless prisms (p. 745).

Section II (p. 746).   *The Reduction of Cryptopine Methochloride in Alkaline Solution.*—The conversion of cryptopine methosulphate into tetrahydromethylcryptopine by reduction in strongly acid
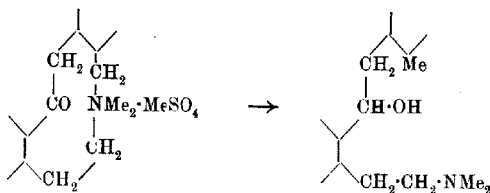
solution with sodium amalgam is described in Part I of this research (821 and 826), and the present object was to determine whether, during this process, the reduction of the keto-group precedes the fission of the ring or vice versâ.   Since further experiments on the reduction of the methosulphate did not yield information of value, the effect of reducing agents on the corresponding methochloride was investigated.   The interesting fact was then observed that, whilst cryptopine methochloride, when reduced in alkaline solution with sodium amalgam, is converted in the

main into tetrahydromethylcryptopine, there is also formed in small quantity a new base, $C_{22}H_{27}O_5N$, which melts at 118—120°, and is obviously produced according to the scheme:

Dihydromethylcryptopine.
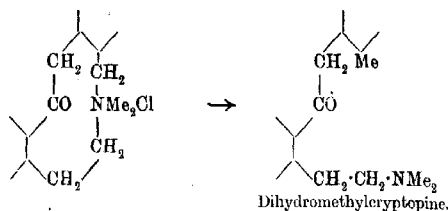
that is to say, during its formation, the ten-membered ring has been ruptured before the reduction of the keto-group.

The constitution assigned to dihydromethylcryptopine receives support from the fact that, when oxidised with permanganate, the base yields 5 : 6-methylenedioxy-o-tolualdehyde and 5 : 6-methylene-dioxy-o-toluic acid (compare p. 747). The isolation of this base would seem to indicate that the first action of the alkaline reducing agent on cryptopine methochloride is fission of the ten-membered ring, but that most of the dihydromethylcryptopine, thus produced, suffers further reduction before it can be removed from the sphere of action of the excess of the reducing agent.

Section III.

The Reduction of isoCryptopine Chloride.

In the cases discussed in Sections I and II, the groups of atoms taking part and suffering disruption as the result of reduction belong in I to a single dihydroisoquinoline nucleus, and in II to the ten-membered group characteristic of cryptopine:

(I.)   (II.)
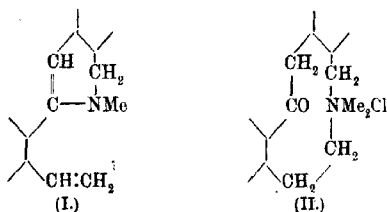
It was next desired to investigate what the effect of reduction might be in the case of a substance containing a partly reduced double isoquinoline ring, and isocryptopine chloride (833) was

$$\begin{array}{c} \text{CH} \quad \text{CH}_2 \\ \parallel \quad \mid \\ \text{C----NMeCl} \\ \mid \\ \text{CH}_2 \\ \text{CH}_2 \end{array}$$
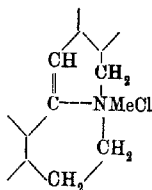
selected for this purpose. The effect of reduction was again studied (a) in alkaline and (b) in acid solution.

Section III (a). The Reduction of iso*Cryptopine Chloride in Alkaline Solution* (p. 748).—Since *iso*cryptopine chloride is very sparingly soluble in cold water, the reduction with sodium amalgam could only be carried out effectively on the steam-bath, and, under these conditions, a resinous base separates, and the liquid, on cooling, becomes filled with a voluminous mass of needles of a quaternary salt. This salt, which is produced in considerable quantity, was readily identified as *iso*dihydrocryptopine β-chloride, since, on boiling with methyl-alcoholic potassium hydroxide, it yielded anhydrodihydrocryptopine (*A*) (938):

$$\begin{array}{c} \text{CH}_2 \quad \text{CH}_2 \\ \mid \quad\quad \mid \\ \text{CH---NMeCl} \\ \mid \\ \text{CH}_2 \\ \text{CH}_2 \end{array} \quad \rightarrow \quad \begin{array}{c} \text{CH} \quad \text{CH}_2 \\ \parallel \quad\quad \mid \\ \text{CH} \quad \text{NMe} \\ \mid \\ \text{CH}_2 \\ \text{CH}_2 \end{array} \quad .$$
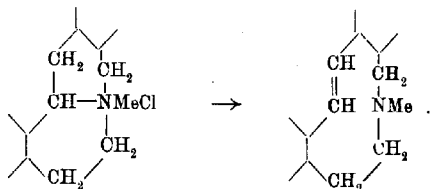
One of the main directions in which *iso*cryptopine chloride suffers reduction is therefore simply by the addition of hydrogen to the double linking without disruption of either ring. The resinous base may be separated, by fractional crystallisation, into two new substances, namely, a very sparingly soluble base, $C_{21}H_{23}O_4N$, melting at 195°, which is present in very small quantity, and considerable quantities of a readily soluble base, $C_{21}H_{25}O_4N$, which melts at 138°. The base, $C_{21}H_{23}O_4N$, yields, on oxidation, 5 : 6-methylenedioxy-*o*-toluic acid (916), and apparently

$$\begin{array}{c} \text{O} \\ \text{O} \end{array}\!\!>\!\text{CH}_2 \qquad \text{and} \qquad \begin{array}{c} \text{CO} \\ \text{MeO} \quad \text{NMe} \\ \text{MeO} \quad \text{CH}_2 \\ \text{CH}_2 \end{array}$$

with Me, CO₂H labels

E E*
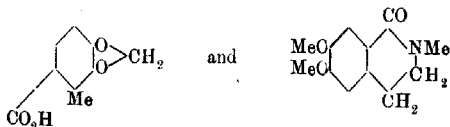
also 1-keto-6:7-dimethoxy-2-methyltetrahydro*iso*quinoline (Pyman, T., 1909, **95**, 1268), and must therefore have the constitution

$$
\begin{array}{c}
\text{CH} \quad \text{Me} \\
\| \\
\text{C} \!-\!\!-\! \text{NMe} \\
\diagdown \qquad | \\
\qquad \text{CH}_2 \\
\diagdown \text{CH}_2 \diagup
\end{array}
$$
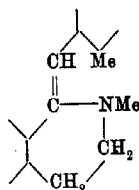
Dihydroanhydro*iso*cryptopine.

This base is therefore produced from *iso*cryptopine chloride by the rupture of the upper dihydro*iso*quinoline ring without reduction of the double linking.

The readily soluble base, $C_{21}H_{25}O_4N$, melting at 138°, yields 5:6-methylenedioxy-*o*-tolualdehyde (and acid), as well as 1-keto-6:7-dimethoxy-2-methyltetrahydro*iso*quinoline, on oxidation with permanganate, and must therefore be the dihydro-derivative of the base just described (m. p. 195°) and have the constitution

$$
\begin{array}{c}
\text{CH}_2 \quad \text{Me} \\
| \\
\text{CH} \!-\!\!-\! \text{NMe} \\
\diagdown \qquad | \\
\qquad \text{CH}_2 \\
\diagdown \text{CH}_2 \diagup
\end{array}
$$
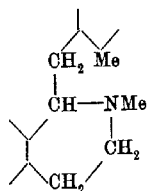
Tetrahydroanhydro*iso*cryptopine.

It yields very characteristic salts and other derivatives, of which the *methosulphate*, $C_{21}H_{25}O_4N,Me_2SO_4$ (m. p. 160°), and *meth-iodide*, $C_{21}H_{25}O_4N,MeI$ (m. p. 263°), crystallise particularly well. When boiled with methyl-alcoholic potassium hydroxide, the methosulphate is readily decomposed, with the formation of anhydrotetrahydromethylcryptopine, a base which had previously

$$
\begin{array}{c}
\text{CH}_2 \quad \text{Me} \\
| \\
\text{CH} \!-\!\!-\! \text{NMe}_2 \cdot \text{OH} \\
\diagdown \qquad | \\
\qquad \text{CH}_2 \\
\diagdown \text{CH}_2 \diagup
\end{array}
\qquad \longrightarrow \qquad
\begin{array}{c}
\text{CH} \quad \text{Me} \\
\| \\
\text{CH} \\
\diagdown \\
\diagdown \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2
\end{array}
$$
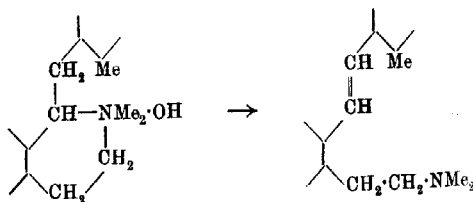
been obtained, in the form of its hydrochloride, from tetrahydromethylcryptopine by the action of phosphoryl chloride (899).

Section III (b). *The Reduction of* iso*Cryptopine Chloride in Acid Solution* (p. 749).—Reduction takes place readily when the *hot solution of *iso*cryptopine chloride in a mixture of dilute acetic and hydrochloric acids is treated with a large excess of sodium amalgam, and leads to the formation of two bases, $C_{21}H_{25}O_4N$, melting at 138° and 164° respectively, as well as of considerable quantities of *iso*dihydrocryptopine β-chloride.

The base melting at 138° is tetrahydroanhydroiso*cryptopine, identical with that isolated from the product of the alkaline reduction of *iso*cryptopine chloride. The second base, melting at 164°, which does not appear to be one of the products of the alkaline reduction, is *dihydroanhydrodihydrocryptopine* (A), and, in its formation, not only has the ethenoid linking in *iso*cryptopine been reduced, but the double *iso*quinoline ring has also suffered disruption in a very remarkable manner, with the formation of a fully saturated ten-ring system.

Dihydroanhydrodihydrocryptopine (A).
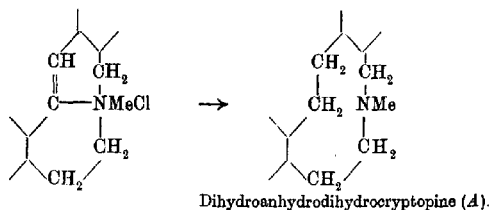
This base is remarkably stable to permanganate, and does not yield 5 : 6-methylenedioxy-*o*-toluic acid on oxidation, showing that reduction has not resulted in the formation of the group $CH_2:O_2:C_6H_2Me\cdot CH:$ (p. 716).

The definite proof of its constitution was obtained as the result of the observation that the base in question is readily produced when anhydrodihydrocryptopine (A) (938) is reduced by sodium amalgam in acid solution.
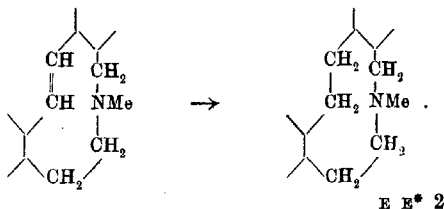
The curious formation of dihydroanhydrodihydrocryptopine (A) from *iso*cryptopine chloride by reduction is dependent in some way on the presence of the ethenoid linking in one of the reduced *iso*quinoline rings, a condition which apparently causes strain, and consequent instability. That this is so is indicated by the facts that, when this ethenoid linking is not present, scission does not appear to take place. Thus, for example, all attempts to reduce tetrahydroberberine methochloride, which contains the grouping

$$CH_2 \quad CH_2$$
$$CH-NMeCl \ ,$$
$$CH_2$$
$$CH_2$$
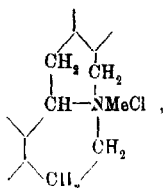
have been unsuccessful.

Dihydroanhydrodihydrocryptopine (A) yields a methosulphate, $C_{21}H_{25}O_4N,Me_2SO_4$, which, on hydrolysis with methyl-alcoholic potassium hydroxide, is converted into *dihydro*isoanhydrodihydromethylcryptopine, $C_{22}H_{27}O_4N$ (945), a beautiful substance melting at 77°, the crystals of which have been measured (p. 757).

$$CH_2 \quad CH_2$$
$$CH_2 \quad NMe_2 \cdot OH \quad \rightarrow \quad CH_2 \quad NMe_2$$
$$CH_2$$
$$CH_2 \qquad\qquad CH:CH_2$$
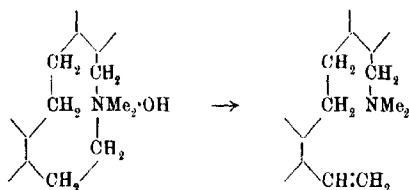
Finally, the methosulphate of this base, $C_{22}H_{27}O_4N,Me_2SO_4$, is decomposed by boiling with methyl-alcoholic potassium hydroxide, with the separation of *dihydro*-α-isocryptopidol,

$$CH_2 \quad CH_2 \cdot OH$$
$$CH_2$$
$$CH:CH_2$$
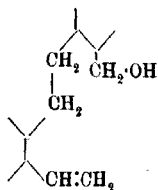
a rather indefinitely crystalline substance which is clearly the dihydro-derivative of α-*iso*cryptopidol (948).

Section III (c). Dihydroanhydrotetrahydromethylcryptopine (p. 759).—This substance is produced from the methosulphate either of tetrahydroanhydroisocryptopine (I, m. p. 138°, p. 722) or of dihydroanhydrodihydrocryptopine (A) (II, m. p. 164°, p. 723) by reduction in alkaline solution with sodium amalgam:

CH₂ Me
CH—NMe₂·OH
CH₂
CH₂
(I.)

CH₂ Me
CH₂
CH₂·CH₂·NMe₂
Dihydroanhydrotetrahydro-
methylcryptopine.

CH₂ CH₂
CH₂ NMe₂·OH
CH₂
CH₂
(II.)
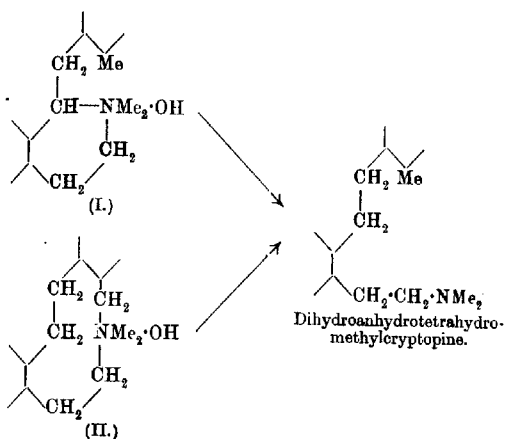
The other cases of ring-fission during reduction, described in this communication, occur in systems in which the ring in question is unsaturated, and it is pointed out on p. 724 that attempts to reduce the completely saturated system,

CH₂ CH₂
CH—NMeCl ,
CH₂
CH₂
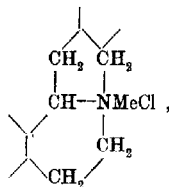
contained in tetrahydroberberine methochloride, have not been successful.

It is therefore remarkable that the removal of a bridge in this complex in the two directions shown in formulæ I and II should so weaken the structure as to make it susceptible to reduction. It is, of course, possible that the accumulation of methyl groups on the nitrogen atom may tend to weaken the structure, and a good

deal of evidence is to be found in this communication·in favour
of that view.

Dihydroanhydrotetrahydromethylcryptopine melts at 63°, and is
characterised by yielding a very sparingly soluble hydrochloride.
The *methosulphate*, $C_{22}H_{29}O_4N,Me_2SO_4$, is decomposed by boiling
with methyl-alcoholic potassium hydroxide, with elimination of
trimethylamine and formation of *dihydrocryptopidene*.
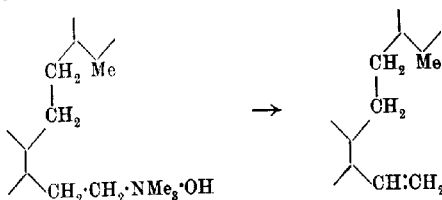
This new derivative of cryptopidene (926) crystallises splendidly,
melts at 126—128°, and yields the following interesting substances
on oxidation with permanganate:

Ketodihydrocryptopidene.   Dihydrocryptopidenic acid.
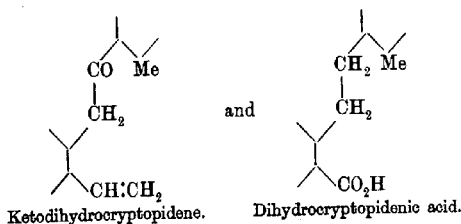
Ketodihydrocryptopidene melts at 116° and yields a *semicarbazone*,
$C_{21}H_{23}O_5N_3$, melting at 190°. *Dihydrocryptopidenic acid* is a very
sparingly soluble, crystalline acid (m. p. 194—195°), the *anilide*
of which, $C_{18}H_{19}O_4 \cdot CO \cdot NH \cdot C_6H_5$, crystallises in needles and melts
at 185°.

The degradation of cryptopine to this acid is particularly
interesting, and it is unfortunate that the small amount of material
available did not allow of its detailed investigation.

Section IV.

The Reduction of ψ-Cryptopine Chloride.

The conversion of anhydrocryptopine methosulphate into
ψ-cryptopine chloride is mentioned on p. 715 (compare 855 and
984), and the similarity in constitution between this substance and

*iso*cryptopine chloride is obvious when their formulæ are compared :

isoCryptopine chloride.   ψ-Cryptopine chloride.
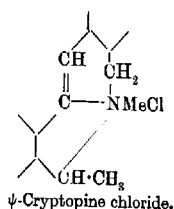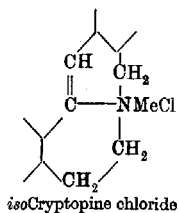
The essential difference between these formulæ is the fact that, whereas in *iso*cryptopine chloride the central portion consists of two reduced *iso*quinoline rings fused together, the molecule of ψ-cryptopine chloride contains only one such ring. When the bridge across the molecule is removed by reduction, the result in the case of *iso*cryptopine chloride is the formation of a ten-membered ring (p. 723), whereas if a similar change is assumed to take place in the molecule of ψ-cryptopine chloride, reduction should lead to the formation of a nine-membered ring system, of which, so far, few examples have been described.

Since the investigation of this matter seemed to offer attractive possibilities, the problem has been carefully studied, and it may be said at once that the comparatively slight difference in constitution which ψ-cryptopine chloride exhibits in comparison with *iso*cryptopine chloride is sufficient to give rise to wide differences in behaviour when the two substances are reduced under similar conditions.

Section IV (a). *The Reduction of ψ-Cryptopine Chloride in Alkaline Solution* (p. 769).—ψ-Cryptopine chloride, $C_{21}H_{22}O_4NCl$, is readily reduced in slightly alkaline aqueous solution by sodium amalgam at the temperature of the steam-bath, and a base, $C_{21}H_{23}O_4N$, separates, which crystallises from methyl alcohol in stout prisms and melts at 112°.*

This base is produced by the addition of two atoms of hydrogen to ψ-cryptopine chloride and elimination of hydrogen chloride, a

---

* In the reduction of *iso*cryptopine chloride, much *iso*dihydrocryptopine β-chloride is always obtained by the direct reduction of the ethenoid linking (p. 721), but the corresponding *iso*dihydro-ψ-cryptopine chloride does not appear to be one of the products of the reduction of ψ-cryptopine chloride. Still more striking is the observation that, whereas during the reduction of *iso*cryptopine chloride, the base formed in much the larger quantity is tetra-hydroanhydro*iso*cryptopine, $C_{21}H_{25}O_4N$, in the case of ψ-cryptopine chloride the reduction does not appear to proceed beyond the formation of the base $C_{21}H_{23}O_4N$ (m, p, 112°).

process which might take place in two different directions, leading to the formulæ

(I.)   and   (II.)
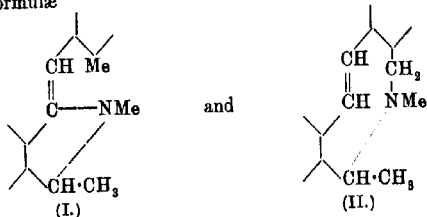
Judging from the course the reduction takes in the analogous case of *iso*cryptopine chloride, the new base should correspond in constitution with dihydroanhydroisocryptopine (m. p. 195°, p. 722), that is to say, it should have the constitution represented by the partial formula I.

The investigation of the base has, however, shown that this is not the case. It does not, for example, yield 5 : 6-methylenedioxy-*o*-toluic acid, $CH_2:O_2:C_6H_2Me\cdot CO_2H$ (p. 721), on oxidation with permanganate, and it can therefore scarcely contain the grouping, $CH_2:O_2:C_6H_2Me\cdot CH:$, which is present in I. The alternative is that its constitution is that represented by formula II, and for this reason the base, $C_{21}H_{23}O_4N$, melting at 112°, has been named *ψ-anhydrodihydrocryptopine* (*A*) to indicate its relationship to anhydrodihydrocryptopine (*A*) (841). This base combines readily with methyl sulphate, and both the methosulphate,
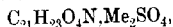
$$C_{21}H_{23}O_4N,Me_2SO_4,$$

and the corresponding methiodide, $C_{21}H_{23}O_4N,MeI$, are beautifully crystalline substances characterised by yielding highly coloured products on decomposition with methyl-alcoholic potassium hydroxide, which are obviously of complex nature and have not been further investigated.

When, however, the alkaline solution of the methosulphate is reduced by sodium amalgam, a remarkable change takes place, and a neutral substance, $C_{20}H_{20}O_4$, separates:

$$C_{20}H_{20}O_4NMe_2\cdot OH + 2H = C_{20}H_{20}O_4 + NHMe_2 + H_2O.$$
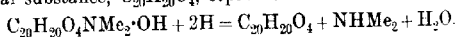
It is probable that this curious decomposition takes place in the following direction:
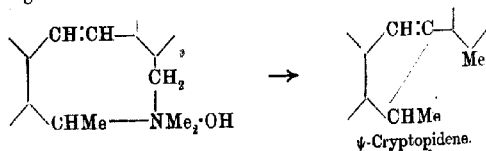
ψ-Cryptopidene.

and, since the new substance, which crystallises beautifully and melts at 144°, is isomeric with cryptopidene (926; compare p. 772), it has been named ψ-*cryptopidene*.

An attempt was made to establish the constitution of the substance by studying its behaviour on oxidation with permanganate, but with partial success only. One of the substances produced is 5:6-methylenedioxy-o-toluic acid, the formation of which is in harmony with the suggested constitution. The principal products of oxidation are, however, *dioxy-ψ-cryptopidene*, $C_{20}H_{18}O_6$ (m. p. 138—140°), and *trioxy-ψ-cryptopidene*, $C_{20}H_{18}O_7$ (m. p. 165°). Both these substances exhibit a reaction reminiscent of the benzil reaction, that is to say, on boiling with methyl-alcoholic potassium hydroxide they dissolve to brown solutions which, in contact with air, become pink and gradually fade; the addition of hydrochloric acid then causes the precipitation of crystalline acids. Dioxy-ψ-cryptopidene yields a *semicarbazone*, $C_{21}H_{21}O_6N_3$, and trioxy-cryptopidene a *disemicarbazone*, $C_{22}H_{24}O_7N_6$, so that if the formula assigned to ψ-cryptopidene is correct, it is probable that these oxidation products may have the partial formulæ
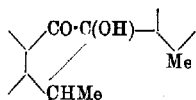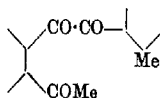
Dioxy-ψ-cryptopidene. and Trioxy-ψ-cryptopidene.

Section IV (b). *The Reduction of ψ-Cryptopine Chloride in Acid Solution* (p. 774).—It has just been explained that the methosulphate of ψ-anhydrodihydrocryptopine (A) undergoes a curious decomposition when it is reduced in alkaline solution, with loss of the nitrogen atom as dimethylamine and formation of a neutral substance, $C_{20}H_{20}O_4$ (ψ-cryptopidene).

It is perhaps still more remarkable that ψ-cryptopine chloride itself should, on reduction in acid solution with sodium amalgam, undergo a partial change in a similar direction, with elimination of the nitrogen atom, evidently as methylamine, and separation of a beautifully crystalline substance, $C_{20}H_{20}O_4$, which is isomeric with ψ-cryptopidene (m. p. 144°), melts at 152°, and has been named iso-ψ-*cryptopidene*. Since the melting points of the two substances do not greatly differ, it was at first thought that iso-ψ-cryptopidene might possibly be ψ-cryptopidene in a very pure condition; but this is not the case, because the mixture of the two substances melts at about 130°. On oxidation with permanganate, iso-ψ-cryptopidene yields considerable quantities of 5:6-methylenedioxy-o-tolualdehyde (m. p. 72—74°), as well as of the corresponding acid (m. p. 216°; compare p. 777), and also a substance,

$C_{20}H_{20}O_5$ (*ketodihydro*iso-ψ-*cryptopidene*), which melts at 135° and yields a *semicarbazone*, $C_{21}H_{23}O_5N_3$.

The isomerism of ψ-cryptopidene and *iso*-ψ-cryptopidene is difficult to understand, but, as both yield 5 : 6-methylenedioxy-*o*-toluic acid on oxidation, it is suggested that the relationship may be that indicated by the formulæ
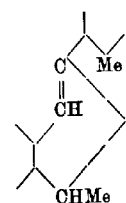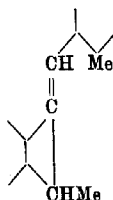
ψ-Cryptopidene.   and   *iso*-ψ-Cryptopidene.

and it is probable that ketodihydro*iso*-ψ-cryptopidene contains the grouping :
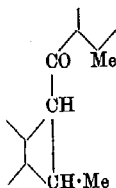
The main product of the reduction of ψ-cryptopine chloride, in acid solution, is a base, $C_{21}H_{25}O_4N$, which is amorphous, but yields a crystalline picrate. Since this base gives 5 : 6-methylenedioxy-*o*-toluic acid on oxidation with permanganate, it is obvious that its constitution must be represented by the partial formula I, and it has therefore been named *dihydroanhydro*-ψ-*cryptopine*. The formation of this base is completely analogous to the conversion of *iso*cryptopine chloride into tetrahydroanhydro*iso*cryptopine (m. p. 138°, p. 722), and the similarity in constitution is clearly exhibited when the partial formulæ are compared :
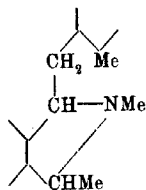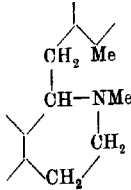
Dihydroanhydro-ψ-cryptopine.   Tetrahydroanhydro*iso*cryptopine.

Section IV (c). *The Reduction of ψ-Methylberberinium Chloride* (p. 778).—In a communication published a short time ago (T., 1918, **113**, 750), it was shown that anhydroberberine methosulphate is converted by the action of hydrochloric acid into a substance called ψ-methylberberinium chloride, which is the analogue in the berberine series of ψ-cryptopine chloride. Since the latter substance exhibits the abnormal behaviour just described when reduced by sodium amalgam in acid solution, it was thought that it would be interesting to investigate the behaviour of ψ-methylberberinium chloride in the same circumstances. The strongly acid solution of ψ-methylberberinium chloride was therefore placed on sodium amalgam, when a neutral substance, $C_{20}H_{20}O_4$ (iso-ψ-*berberidene*), separated, which melts at 117° and exhibits the closest resemblance to *iso*-ψ-cryptopidene. The main product of the reduction was, however, again a base, $C_{21}H_{25}O_4N$ (*dihydroanhydro-ψ-methylberberine*), which, although amorphous, yields a crystalline picrate and hydriodide, and obviously corresponds with the amorphous base—dihydroanhydro-ψ-cryptopine— produced during the reduction of ψ-cryptopine chloride in acid solution.

Section V.

iso*Anhydrocryptopine.*

*iso*Anhydrocryptopine is obtained from anhydrocryptopine by boiling with dilute hydrochloric acid, thus converting it into the isomeric hydroxy*iso*anhydrodihydrocryptopines, and then removing water from the latter by means of phosphoryl chloride (862).

Anhydrocryptopine.

*iso*Anhydrocryptopine.
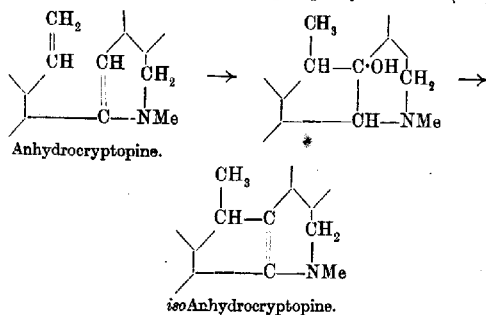
Anhydrocryptopine and *iso*anhydrocryptopine are obviously closely related, since both contain an unsaturated dihydro*iso*quinoline ring methylated at the nitrogen atom. The behaviour of this ring on reduction has been exhaustively studied in the case

of anhydrocryptopine methosulphate (p. 716), with unexpected results, and it seemed possible that additional information of importance might be obtained if the behaviour of *iso*anhydro-cryptopine methosulphate were studied under similar conditions.

To some extent, this expectation was realised, but, on the other hand, wide differences, difficult to understand, were found to occur when the behaviour of the products of reduction obtained in the parallel cases to the subsequent action of reducing agents was investigated.

Section V (a).   *The Reduction of* iso*Anhydrocryptopine Metho-sulphate in Alkaline Solution* (p. 782).—This methosulphate is readily reduced at the temperature of the steam-bath, when sodium amalgam acts on its aqueous solution, with the separation of a base, $C_{22}H_{25}O_4N$, which has been named *dihydromethyl*iso*anhydrocrypto-pine*. The examination of this base and its derivatives leaves little doubt that its formation is correctly represented in the following manner:

*iso*Anhydrocryptopine
methohydroxide.

Dihydromethyl*iso*anhydro-
cryptopine.
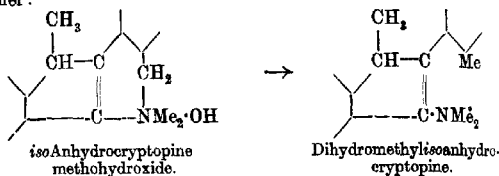
that is to say, it is formed by a process which is analogous to that which occurs when anhydrocryptopine methosulphate is reduced to dihydroanhydromethylcryptopine (p. 716). The new base melts at 122°, and is further characterised by the fact (i) that it exists in well-defined dimorphic modifications (*A*) and (*B*), and (ii) that, on boiling with dilute hydrochloric acid, it undergoes a curious intramolecular change and yields an isomeric base, $C_{22}H_{25}O_4N$ (*ψ-dihydromethyl*iso*anhydrocryptopine*), which melts at 140°.

ψ-Dihydromethyl*iso*anhydrocryptopine.
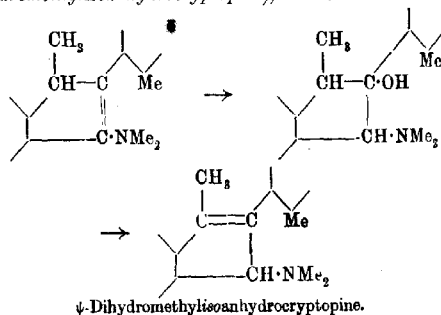
This change is probably due to the addition and subsequent elimination of water, and it is suggested that the process takes place according to the scheme on p. 732.

The occurrence of the grouping, ·CMe:C<, receives support from the observation that ψ-dihydromethyl*iso*anhydrocryptopine is oxidised with unusual difficulty and resists the action of reducing agents in a remarkable degree (p. 788).

The most extraordinary change observed both in the case of dihydromethyl*iso*anhydrocryptopine and its ψ-isomeride is the behaviour of their methosulphates on reduction in alkaline solution by sodium amalgam.

In both cases, trimethylamine is eliminated with great ease, even at the ordinary temperature, and neutral substances, $C_{20}H_{20}O_4$, are produced which are isomeric with and somewhat similar in properties to cryptopidene and the ψ-cryptopidenes (compare pp. 718, 730). Under these conditions, the methosulphate of ψ-dihydromethyl*iso*anhydrocryptopine (m. p. 140°) yields, so far as could be ascertained, a single substance—*iso*cryptopidene (*A*)—melting at 167°, and there is reason to believe that this is formed according to the scheme:

ψ-Dihydromethyl*iso*anhydro-
cryptopine methohydroxide.

*iso*Cryptopidene (*A*).
(M. p. 167°.)
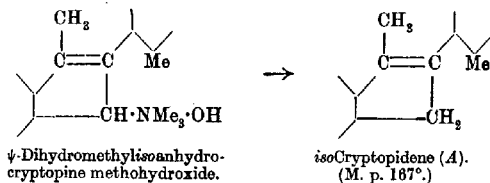
Dihydromethyl*iso*anhydrocryptopine methosulphate behaves in a different manner, yielding two substances, $C_{20}H_{20}O_4$, according to the conditions under which the reduction is carried out. If the aqueous solution of the methosulphate is reduced by sodium amalgam at 30°, decomposition takes place very gradually, and the neutral substance which separates melts at 167°, and is identical with the *iso*cryptopidene (*A*) obtained by the reduction of the methosulphate of the· ψ-isomeride. The boiling aqueous solution of the methosulphate of dihydromethyl*iso*anhydrocryptopine is, however, very rapidly decomposed by crushed sodium amalgam, the neutral substance, $C_{20}H_{20}O_4$, produced melts at 108°, and is therefore isomeric with *iso*cryptopidene (*A*). It has been named *iso*cryptopidene (*B*).

If an attempt is made to explain this puzzling state of things, it

may be suggested that the rapid formation of the substance melt-
ing at ·108° is the direct process,

Dihydromethyl*iso*anhydro-
cryptopine methohydroxide.

*iso*Cryptopidene (*B*).
(M. p. 108°.)
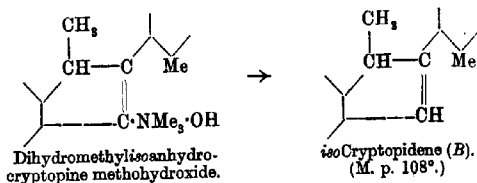
and that during the slow process at 30° the prolonged action of the
alkali causes addition and subsequent elimination of water in the
direction which is assumed to take place during the conversion of
dihydromethyl*iso*anhydrocryptopine into its ψ-isomeride (p. 732).

*iso*Cryptopidene (*A*).
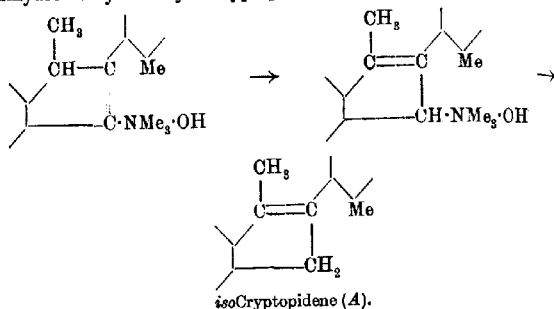
It is, however, obvious that the changes which take place during
these eliminations of trimethylamine are most unusual, and ex-
planations of the course which these decompositions take must
therefore be considered as merely provisional. Some confirmation
of the constitution assigned to *iso*cryptopidene (*B*) is to be found
in its behaviour on oxidation, when it yields a new acid, $C_{20}H_{29}O_5$
(m. p. 227°), which has been named *ketohydroxydihydroisocrypto-
pidenic acid*, and very probably has the constitution
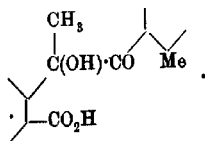
An acid of this constitution could scarcely result from the
oxidation of *iso*cryptopidene (*A*) if the formula assigned to this
substance above is correct.

One of the most remarkable decompositions which have been

observed during the course of this long investigation is the process of reduction by sodium amalgam, sometimes in alkaline and sometimes in acid solution, which results in the elimination of the nitrogen atom and separation of a neutral substance, $C_{20}H_{20}O_4$. This change has been observed in the following cases:
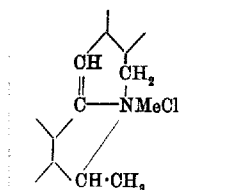
ψ-Cryptopine chloride and ψ-methylberberinium chloride. (I.)
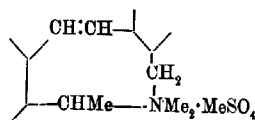
ψ-Anhydrodihydrocryptopine (A) methosulphate. (II.)
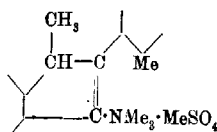
Dihydromethyl*iso*anhydro-cryptopine methosulphate. (III.)
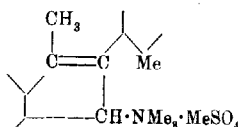
ψ-Dihydromethyl*iso*anhydro-cryptopine methosulphate. (IV.)

nd the nitrogen atom is eliminated as methylamine in (I), as imethylamine in (II), and as trimethylamine in (III) and (IV). ln the other hand, substances very similar in constitution to those gured above, such, for example, as
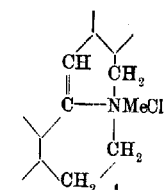
*iso*Cryptopine chloride.
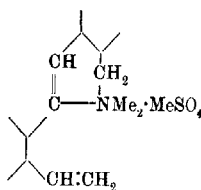
Anhydrocryptopine methosulphate.
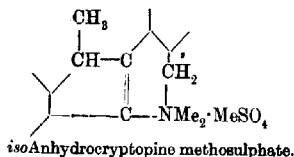
*iso*Anhydrocryptopine methosulphate.

do not lose the nitrogen atom when subjected to the action of sodium amalgam under the same conditions.

This matter is obviously very complex and difficult to understand, and, at the present stage, is seems impossible to form any idea as to the conditions which cause the nitrogen atom to be in so reactive a state that it is readily removed by the action of sodium amalgam, sometimes at the ordinary temperature. If opportunity occurs, it is proposed to study the mechanism of changes of this kind in the case of *iso*quinoline derivatives and other analogous substances of less complex structure than the substances discussed in the present communication.

EXPERIMENTAL.

Preparation of Anhydrocryptopine Methosulphate,
$C_{21}H_{21}O_4N,Me_2SO_4$.

It has already been pointed out that the process previously given (978) for the preparation of this substance is unsatisfactory, and, as considerable quantities of this valuable material were required for the purpose of the present investigation, comparative experiments were instituted, and finally the following conditions were found to give a yield of more than 80 per cent. of that theoretically possible.

The anhydrocryptopine employed was prepared from *iso*cryptopine chloride substantially according to the method already described (975), but it is not necessary to use more than 20 c.c. of 25 per cent. methyl-alcoholic potassium hydroxide for each 10 grams of the chloride. The product was washed thoroughly at the pump, first with water, then several times with methyl alcohol, in which anhydrocryptopine is very sparingly soluble, and finally with water. The pale yellow product was left in contact with porous porcelain until air-dry, then dried at a temperature not exceeding 80° * until no further loss in weight occurred ; finally, it was powdered and passed through a very fine sieve. Prepared in this way, anhydrocryptopine is nearly pure and melts at about 108—110° ; it contains, at the most, traces of inorganic matter and of *iso*cryptopine chloride.

In order to prepare the methosulphate, anhydrocryptopine (10 grams) is shaken in a corked flask with excess of freshly distilled

* If the temperature is allowed to rise to 95—100°, the mass soon becomes brown and viscid and rapidly decomposes, a change which appears to be mainly the result of oxidation. For the successful preparation of the methosulphate, anhydrocryptopine must be quite dry.

methyl sulphate (10 c.c.), when a paste is formed and there is no apparent immediate action. On keeping, the paste rapidly thickens, and in two days will have set to a hard cake. After remaining for four days, the flask is broken, and the cake crushed and washed at the pump with benzene, which removes the excess of methyl sulphate and colouring matter.*

The dry, pale yellow residue is left on porous porcelain until the adherent benzene has evaporated; it then weighs 11 grams, and is dissolved in boiling methyl alcohol, from which the pure methosulphate separates, on slowly cooling, in brilliant sulphur-yellow prisms, and melts at 238—240°, as previously stated. The measurement of some fine crystals of anhydrocryptopine methosulphate was kindly undertaken by Miss M. Porter, with the following result:

The crystals are monoclinic with axial ratios $a:b:c = 1\cdot504:1: 0\cdot931$, $\beta = 104°15'$, the forms observed being $a\{100\}$, $m\{110\}$, $c\{001\}$, $r\{1\overline{0}1\}$, and $e\{102\}$. The habit is tabular parallel to $c(001)$, and very much elongated along the b-axis, as shown in Fig. 1. The form $c\{001\}$ is the predominant terminating form; $r\{1\overline{0}1\}$ is well developed, and $e\{102\}$, when present, is very narrow. The crystals gave poor reflections; three were measured, and the results are placed in the table below.

No. of read-ings.		Azimuth (ϕ).			Polar distance (ρ).		
Face.	ings.	Limits.	Obs.	Calc.	Limits.	Obs.	Calc.
a (100)	4	89°55'—90° 5'	90° 1'	90°0'	90° 0'—90° 0'	90° 0'	90° 0'
m (110)	4	34 30 —34 42	*34 34	—	90 0 —90 0	90 0	90 0
c (001)	3	87 25 —90 35	88 47	90 0	15 48 —16 2	*15 15	—
r (101)	3	87 45 —90 15	89 33	90 0	19 53 —20 30	*20 15	—
e (102)	1	—	90 41	90 0	—	30 30	30 40

Determinants : 010/001/100. Complex-symbol : 4h; $-15/64\frac{1}{2}/+2$.

FIG. 1.

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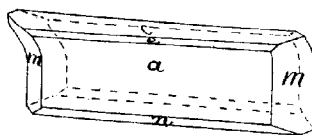
* A quicker process is to dissolve the cake in boiling methyl alcohol, from hich the methosulphate separates, on cooling, in an almost pure condition. he yield, however, is not so good as that obtained after extraction with enzene. This is probably due to the fact that the solution in boiling methyl cohol, containing the excess of methyl sulphate, rapidly becomes very acid, d this causes some decomposition of the methosulphate.

The methyl-alcoholic mother liquors of the pure methosulphate yielded, on concentrating, a further crop of less pure methosulphate, and, on concentrating further and leaving in the ice-chest, a mass of soft, yellow, nearly square plates separated, together with a few of the large prisms of the methosulphate. The two substances were easily separated by means of a sieve, and the second substance, after recrystallisation from water, proved to be *anhydrocryptopine methyl hydrogen sulphate*:

0·1181 gave 0·2471 CO_2 and 0·0582 H_2O. $C = 57·2$; $H = 5·5$.

$C_{21}H_{21}O_4N.MeHSO_4$ requires $C = 57·0$; $H = 5·4$ per cent.

The most striking difference between the methosulphate and this salt lies in the fact that, whereas the solution of the former gives no precipitate with ammonia, the addition of ammonia to that of the latter causes the immediate separation of a caseous precipitate which, after crystallisation from methyl alcohol, melts at 110—111°, and consists of anhydrocryptopine.

Oxidation of Anhydrocryptopine Methochloride to Dioxymethyl-

isoanhydrodihydrocryptopine (945),

$$\begin{array}{c} \diagup \diagup \diagdown \\ CH \cdot OH \quad CH_2 \\ | \qquad\quad | \\ CO \qquad\quad NMe_2 \\ \diagup \diagdown \\ CH{:}CH_2 \end{array}$$
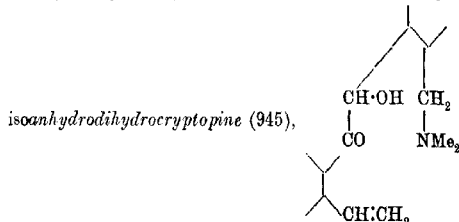
This oxidation was carried out by dissolving anhydrocryptopine methochloride (5 grams; compare 981) in water (1 litre), and, after cooling in ice and salt until the solution was partly frozen, cold saturated permanganate (containing 5·5 grams of $KMnO_4$) was gradually added with mechanical stirring. The permanganate was immediately decolorised, and, when the operation was complete, the whole was heated to boiling, filtered, and the brown filtrate concentrated to half its bulk, during which a small quantity of a crystalline substance separated. After two days, this was collected (0·5 gram), and a second small quantity was obtained by further concentrating the deep brown filtrate, the total yield being 0·67 gram. On still further concentrating, the odour of dimethylamine became apparent, and all attempts to obtain anything crystalline from the tar which resulted were unsuccessful. The crystalline substance (0·67 gram) is sparingly soluble in cold

alcohol and not very readily so on boiling, and separates in drab needles. After twice recrystallising, the following analytical details were obtained with different preparations:

0·1129 gave 0·2724 CO_2 and 0·0633 H_2O. C = 65·8 ; H = 6·2.

0·1026 „ 0·2496 CO_2 „ 0·0596 H_2O. C = 66·3 ; H = 6·4.

$C_{22}H_{25}O_6N$ requires C = 66·2 ; H = 6·3 per cent.

Dioxymethylisoanhydrodihydrocryptopine melts at 187—188°, and is sparingly soluble in benzene or acetone in the cold and nearly insoluble in light petroleum. It dissolves in boiling acetone and separates in glistening balls of needles. The substance is a strong base, dissolves immediately in cold dilute hydrochloric acid, and gives, on the addition of ammonia, a milky liquid and an amorphous precipitate which, on warming, becomes crystalline. The sulphate and nitrate, like the hydrochloride, are readily soluble. The addition of platinic chloride to the dilute solution of the hydrochloride produces an ochreous precipitate, which melts to a green oil under boiling water, and the supernatant liquid becomes first green and then brown. Auric chloride produces, with a dilute solution of the hydrochloride, a pale chocolate precipitate, soluble in hot water, and, on boiling, the liquid becomes green and deposits a purple precipitate of reduced gold. When a few drops of copper sulphate are added to the solution of the hydrochloride, a pale yellowish-green solution is obtained which, on boiling, becomes first deep blue, then yellow, and finally deep reddish-brown ; the addition of alkali then precipitates a reddish-brown precipitate of cuprous oxide.

The solution of the base in ordinary dilute nitric acid becomes deep green when heated at about 80°, and is dichroic with a red reflex ; if the temperature is raised to the boiling point, the intense colour suddenly changes to pale brown, and the odour of nitrous acid develops.

When concentrated nitric acid is poured on to a trace of the substance on a watch-glass, a brilliant orange-red colour is produced, which soon becomes crimson, and then the addition of water gives a crimson solution, which fades to yellow. The solution of the base in glacial acetic acid gives no immediate coloration on the addition of sulphuric acid, but gradually a pink colour develops. If the base is mixed with acetyl chloride in a sealed tube, it becomes crimson, then violet, and finally intense indigo-blue, and, on heating in boiling water, the colour changes to deep green. The whole dissolves completely in water to a brown solution, and ammonia precipitates a chocolate, gelatinous substance which dries to a chocolate-black powder The base does not exhibit the characteristic purple benzoin reaction when it is warmed with

dilute sodium hydroxide or boiled with methyl-alcoholic potassium hydroxide, but, in the latter case, it is converted into a white sub-stance, which is apparently a potassium derivative, and this is decomposed by water with the separation of a white, flocculent precipitate.

The base appears to yield a semicarbazone when it is boiled with excess of semicarbazide hydrochloride and sodium acetate and the product precipitated with ammonia, but the amount of available material was too small for purification and analysis.

Section I (a).   *Reduction of Anhydrocryptopine Methosulphate in Alkaline Solution: Formation of Dihydroanhydromethyl-cryptopine,*
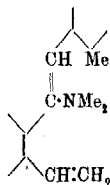
Dihydroanhydromethylcryptopine is obtained when anhydro-cryptopine methosulphate is reduced in alkaline solution by sodium amalgam under the following conditions: The methosulphate (10 grams), dissolved in boiling water (200 c.c.), was poured on crushed sodium amalgam (100 grams of 4 per cent.) in a porcelain beaker, and the whole vigorously stirred, when a base at once separated which adhered to the sides of the beaker and to the glass rod, and hardened on cooling. The mass was ground up, well washed, dis-solved in boiling methyl alcohol, the filtered solution mixed with ether, and the methyl alcohol removed by washing with water. After drying over potassium carbonate, the ethereal solution was concentrated and left for several days in the ice-chest, but, as no crystallisation took place, the ether was evaporated. The hard residue, which resembled colophony, was dissolved in dilute hydrochloric acid and mixed with ammonia, when an amorphous base separated, which was dried over phosphoric oxide in a vacuum desiccator. Two different preparations were analysed :

0·1055 gave 0·2758 CO_2 and 0·0619 H_2O.   C = 71·3 ; H = 6·5.
0·1255 „ 0·3312 CO_2 „ 0·0764 H_2O.   C = 71·9 ; H = 6·8.
$C_{22}H_{25}O_4N$ requires C = 71·9 ; H = 6·8 per cent.

Dihydroanhydromethylcryptopine exhibits no tendency to crystal-lise; its solution in acetic acid gives with sulphuric acid a port

wine coloration, which changes to deep brown on the addition of a drop of dilute nitric acid. The salts are readily soluble, and the solution of the hydrochloride gives, on the addition of potassium iodide, a viscid iodide which dissolves readily in methyl alcohol, but could not be obtained crystalline. The *platinichloride*, prepared by the addition of platinic chloride to the dilute solution of the hydrochloride, is a pale ochreous, chalky precipitate:

0·1265 gave 0·2146 CO_2 and 0·0516 H_2O. C=46·2; H=4·5.

$(C_{22}H_{25}O_4N)_2H_2PtCl_6$ requires C=46·2; H=4·5 per cent.

Oxidation of Dihydroanhydromethylcryptopine.—In order to obtain evidence as to the constitution of this base, the substance (5 grams), dissolved in acetone, was oxidised by the gradual addition of finely powdered permanganate (5·5 grams) at the ordinary temperature. The product was filtered, the manganese precipitate (*A*) well washed with acetone, the filtrate evaporated, and the brown syrup, which had a distinct odour of piperonal, distilled in a current of steam. The cloudy distillate deposited, on keeping in the ice-chest, a large crop of needles which melted at 70—72°, and were recognised as 5:6-methylenedioxy-*o*-tolualdehyde (907).

The residue in the steam distillation flask contained an oil, most of which was soluble in dilute hydrochloric acid, but no further examination was made. The manganese precipitate (*A*) yielded, on extraction with boiling water, a brown solution, which was digested with animal charcoal, concentrated, and acidified, when a solid acid separated and crystallised from glacial acetic acid in colourless needles, melted at 214—216°, and consisted of 5:6-methylenedioxy-*o*-toluic acid (916).

Dihydroanhydromethylcryptopine Methosulphate,
$C_{22}H_{25}O_4N,Me_2SO_4.$
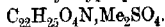
The solution of the base (3 grams) in benzene (15 c.c.) react readily with methyl sulphate (3 c.c.), with development of heat, and in a short time the methosulphate separates as a crystalline mass. This was collected, washed with benzene, and crystallised from water, in which it is rather sparingly soluble in the cold, but readily so on boiling, and from which it separates in colourless groups of prisms:

0·1164 gave 0·2499 CO_2 and 0·0661 H_2O. C=58·5; H=6·3.

$C_{22}H_{25}O_4N,Me_2SO_4$ requires C=58·4; H=6·3 per cent.

This methosulphate melts at 210°, without effervescence, to a slightly coloured syrup; the solution in acetic acid gives with sulphuric acid a deep cherry-red coloration which, on the addition

of a drop of dilute nitric acid, changes to brownish-violet. The corresponding *methiodide*, $C_{22}H_{25}O_4N,MeI$, is obtained by adding hot dilute potassium iodide to the hot dilute solution of the metho-sulphate, when a milky liquid is produced, which soon deposits glistening spangles:

0·1123 gave 0·2242 CO_2 and 0·0559 H_2O.   C=54·4; H=5·5.

$C_{22}H_{25}O_4N,MeI$ requires C=54·2; H=5·5 per cent.

This iodide is remarkably stable, it scarcely darkens at 200°, and melts at about 217° with very little decomposition.

Hydroxycryptopidene (compare 926),
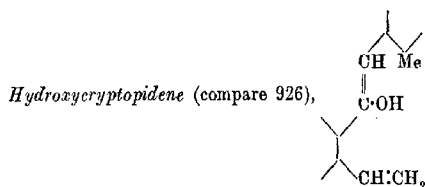
This interesting substance, isomeric and closely allied in proper-ties with α-*iso*cryptopidol (m. p. 90—92°; 948), is obtained when dihydroanhydromethylcryptopine methosulphate is decomposed by methyl-alcoholic potassium hydroxide. The methosulphate (7 grams), dissolved in hot methyl alcohol, was mixed with methyl-alcoholic potassium hydroxide (60 c.c. of 25 per cent.) and heated to boiling, when trimethylamine was immediately eliminated, but decomposition was nevertheless slow.

After an hour, most of the methyl alcohol was evaporated, and the pasty residue heated in boiling water for two hours; water was then added, and the viscid precipitate extracted with much ether. The ethereal solution, which contained a flocculent precipitate consisting apparently of a polymeric modification of hydroxy-cryptopidene (compare below), was filtered, thoroughly washed with dilute hydrochloric acid, dried over potassium carbonate, and con-centrated, when, on remaining for several days in the ice-chest, a crust of nodules separated which melted at 88—89°, and consisted of pure hydroxycryptopidene. As the amount which had separated was only small, the ethereal mother liquor was evaporated, when a pale brown syrup remained which soon began to crystallise in nodules, and crystallisation was much facilitated by trituration with methyl alcohol, in which the substance is sparingly soluble. After collecting and washing with methyl alcohol, the colourless residue was recrystallised from methyl alcohol, from which hydr-oxycryptopidene separates in circular nodules melting at 87—89°. Two different preparations were analysed:

0·1272 gave 0·3288 CO_2 and 0·0704 H_2O. C=70·4; H=6·1.

0·1289 ,, 0·3336 CO_2 ,, 0·0701 H_2O. C=70·5; H=6·1.

$C_{20}H_{20}O_5$ requires C=70·6; H=5·9 per cent.

Hydroxycryptopidene is very readily soluble in benzene, but sparingly so in ether or cold, light petroleum. It dissolves, however, moderately readily in the latter solvent on boiling, and separates in well-developed chisel-shaped prisms and also in single lenticular prisms.

Hydroxycryptopidene dissolves in acetyl chloride in the cold with some development of heat, and, when heated in a sealed tube, the solution becomes purple, then bluish-violet, and finally deep indigo-blue. When the product is evaporated on the steam-bath, a blue resin remains, which loses its colour on boiling with methyl alcohol, and a chalky substance separates. This was collected, washed with methyl alcohol, in which it is nearly insoluble, and purified by dissolving in glacial acetic acid and precipitating with methyl alcohol. After washing with methyl alcohol, the chalky residue contained 4·98 per cent. of chlorine, and this was removed by boiling with 10 per cent. methyl-alcoholic potassium hydroxide. The precipitate was then collected, washed well with methyl alcohol, then with water, dissolved in glacial acetic acid, and precipitated by methyl alcohol :

0·1158 gave 0·3005 CO_2 and 0·0603 H_2O. C=70·8; H=5·8.

$C_{20}H_{20}O_5$ requires C=70·6; H=5·9 per cent.

Clearly the action of the acetyl chloride had been, not to produce an acetyl derivative, but to convert the hydroxycryptopidene into a polymeric modification, which, since it closely resembles β-isocryptopidol (947), may be named *hydroxyisocryptopidene* (β). This polymeride shrinks at 175—180° and froths up at about 200°.

Section I (b). *Reduction of Anhydrocryptopine Methosulphate in Acid Solution: Formation of Tetrahydroanhydromethylcryptopine,*
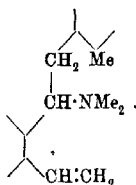
In preparing tetrahydroanhydromethylcryptopine, anhydrocryptopine methosulphate (5 grams), dissolved in warm water

(100 c.c.) and dilute hydrochloric acid (5 c.c.), was poured on
sodium amalgam in a flat basin, and then hydrochloric acid
(20 c.c.) gradually added, so that the whole always remained dis-
tinctly acid.* As soon as the amalgam was exhausted, the liquid
was filtered from a small quantity of a viscid substance insoluble
in dilute hydrochloric acid, mixed with excess of ammonia, and
the milky product extracted with ether. The ethereal solution
was washed with water, dried over potassium carbonate, and con-
centrated, and, as no crystallisation had taken place after remain-
ing for a week in the ice-chest, the ether was evaporated. The
gummy residue was then dissolved in dilute hydrochloric acid, pre-
cipitated by ammonia, and, after collecting and washing, the base
was dried in a vacuum desiccator over phosphoric oxide : ·

0·1140 gave 0·2972 CO_2 and 0·0757 H_2O. C=71·1; H=7·4.

$C_{22}H_{27}O_4N$ requires C=71·5; H=7·3 per cent.

Tetrahydroanhydromethylcryptopine, isomeric with anhydro-
tetrahydromethylcryptopine (m. p. 107°; 898), has not been
obtained in a crystalline condition.

It is readily soluble in dilute hydrochloric acid, and the addition
of concentrated hydrochloric acid produces a milky liquid, from
which the hydrochloride separates as a syrup. The *platinichloride*,
prepared in the usual manner, is an ochreous precipitate some-
what soluble in hot water, from which it separates as a chalky
powder :

0·1175 gave 0·1997 CO_2 and 0·0539 H_2O. C=46·3; H=5·0.

0·4372   ,,   0·0719 Pt.   Pt=16·4.

$(C_{22}H_{27}O_4N)_2,H_2PtCl_6$ requires C=46·1; H=5·0; Pt=16·9 per cent.

Cryptopidene (I) *and Tetrahydrocryptopidene* (II),
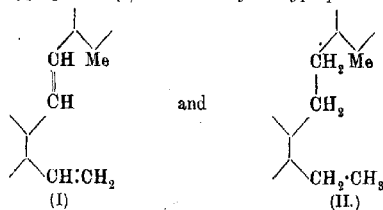
The methosulphate of tetrahydroanhydromethylcryptopine does
not separate when the solution of the base (2 grams) in benzene

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* It is important that the temperature should not rise above 60°, and that
a large excess of hydrochloric acid is not present at any time, otherwise there
is a risk of the formation of considerable quantities of ψ-cryptopine chloride
(compare p. 767).

(5 c.c.) is mixed with methyl sulphate (2 c.c.) and allowed to remain for twenty-four hours.

On the addition of ether, the methosulphate is deposited, how-ever, as a syrup, which on rubbing shows signs of crystallising. The syrup was washed with ether, dissolved in a little methyl alcohol, and boiled with methyl-alcoholic potassium hydroxide (20 c.c. of 30 per cent.), when trimethylamine was eliminated, and, after half an hour, the methyl alcohol was evaporated, the residue mixed with water, and extracted with ether. The ethereal solu-tion, which had a lilac fluorescence, after well washing with dilute hydrochloric acid and drying over potassium carbonate, deposited on evaporation a syrup, which soon crystallised, and contact with porous porcelain removed traces of oily impurity. The colourless residue separated from methyl alcohol in glistening needles exhibit-ing a striking lilac fluorescence, melted at 122—123°, and was recognised as *cryptopidene*. The identity was confirmed by analysis (Found: C = 73·6; H = 6·2. $C_{20}H_{20}O_4$ requires C = 74·1; H = 6·2 per cent.) and by the fact that the mixture with a speci-men of cryptopidene which had previously been obtained from anhydrotetrahydromethylcryptopine methosulphate (926) melted at 120—122°.

Tetrahydrocryptopidene, $C_{20}H_{24}O_4$.—This fine substance is obtained when cryptopidene is reduced in boiling alcoholic solu-tion with sodium, but the change does not take place very readily and completely.

The boiling solution of cryptopidene (5 grams) in alcohol (100 c.c.) was run on to melted sodium (10 grams) contained in a flask fitted with a long condenser and heated in boiling salt solu-tion. Small quantities of boiling alcohol were run in from time to time, and, so soon as all the sodium had dissolved, water was added, the whole extracted with ether, the ethereal solution washed thoroughly, dried, and evaporated, when a crystalline residue remained, which, however, contained unchanged cryptopidene. The reduction was twice repeated exactly as in the first instance, and the product repeatedly recrystallised from methyl alcohol, in which tetrahydrocryptopidene is rather sparingly soluble in the cold, and from which it separates in glistening groups of prisms exhibiting a lilac fluorescence. Considerable difficulty was experi-enced in obtaining accurate analytical results:

0·1236 gave 0·3284 CO_2 and 0·0797 H_2O. C = 72·6; H = 7·2.
0·1142 „ 0·3048 CO_2 „ 0·0750 H_2O. C = 72·7; H = 7·3.
    $C_{20}H_{24}O_4$ requires C = 73·2; H = 7·3 per cent.

Tetrahydrocryptopidene melts at 78°, and is readily soluble in

F F

hot alcohol, acetone, acetic acid, or benzene. It is sparingly soluble in light petroleum (b. p. 60—80°) in the cold, but dissolves readily on boiling, and separates splendidly in stout, well-developed tabular prisms with bevelled edges when the solution is allowed to cool very slowly or to concentrate spontaneously. The solution in acetic acid gives with sulphuric acid an orange-red coloration, which changes to a port wine colour on the addition of a drop of dilute nitric acid. It dissolves in concentrated nitric acid with a striking crimson colour, which soon fades.

Section II.

Reduction of Cryptopine Methochloride in Alkaline Solution.

Dihydromethylcryptopine,

$$CH_2 \cdot Me$$
$$|$$
$$CO$$
$$CH_2 \cdot CH_2 \cdot NMe_2$$
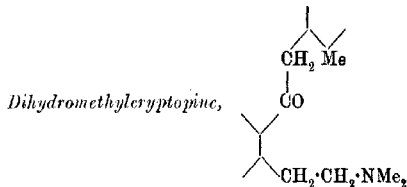
In studying this reduction, the solution of the methochloride (881) (5 grams) in water (100 c.c.) was treated at about 50° with sodium amalgam (100 grams of 4 per cent.), when rapid separation of a viscid, grey base occurred, and the completion of the process was facilitated by heating on the steam-bath. The base was dissolved in methyl alcohol, mixed with much ether, the ethereal solution thoroughly washed with water, dried over potassium carbonate, and concentrated, when, on keeping in the ice-chest, a hard crust of rather indefinite crystals gradually separated, which melted at about 100—102°. The crystals were again dissolved in dry ether, by the aid of methyl alcohol as before, and the rather concentrated liquid then deposited a small quantity of glistening, prismatic needles (0·2 gram) of dihydromethylcryptopine, which became opaque on drying in the steam-oven:

0·1184 gave 0·2977 CO_2 and 0·0757 H_2O.   C=68·6; H=7·1.

$C_{22}H_{27}O_5N$ requires C=68·6; H=7·0 per cent.

Dihydromethylcryptopine melts at 118—120°, and is readily soluble in hot methyl alcohol, but sparingly so in the cold, separating from the hot solution on slowly cooling in glistening, six-sided prisms. When triturated with dilute hydrochloric acid, the base at first becomes viscid, and then the very sparingly soluble hydrochloride forms, which dissolves in boiling dilute hydrochloric

acid and separates as a crust of microscopic prisms. The solution of a trace of the base in a drop of glacial acetic acid gives, with sulphuric acid, a deep reddish-brown coloration.

Oxidation.—The base (0·7 gram), dissolved in acetone (20 c.c.), was oxidised by the gradual addition of very finely powdered permanganate (1·2 grams), but the reduction of the permanganate took place unusually slowly and required two days for completion at the ordinary temperature.

After filtering and washing with acetone, the manganese precipitate was extracted with boiling water, the extract digested with animal charcoal, evaporated to a small bulk, and acidified, when a cloudy liquid was produced, which soon deposited a sparingly soluble, crystalline acid.

This was collected and recrystallised from glacial acetic acid, when it separated in colourless needles melting at 214—216°, which were recognised as 5 : 6-methylenedioxy-o-toluic acid,

$$CH_2{:}O_2{:}C_6H_2Me{\cdot}CO_2H \quad (916).$$
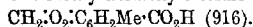
The acetone extract from the oxidation was scarcely coloured, and yielded, on evaporation, a syrup which had the odour of piperonal, and was largely insoluble in dilute hydrochloric acid. On distilling in a current of steam, there separated from the distillate needles which melted at 72—73°, and consisted of 5 : 6-methylenedioxy-o-tolualdehyde, $CH_2{:}O_2{:}C_6H_2Me{\cdot}CHO$ (907).

The ethereal mother liquors from which the dihydromethylcryptopine had separated, as explained above, were concentrated and left for some days in the ice-chest; the hard cake of crystals was then dissolved in dilute hydrochloric acid, and again allowed to remain, when a crust of crystals (0·8 gram) of anhydrotetrahydromethylcryptopine hydrochloride, $C_{22}H_{27}O_4N,HCl$ (900), separated. This sparingly soluble hydrochloride was removed by filtration, the filtrate made strongly alkaline with ammonia, and the viscid base extracted with ether. After drying over potassium carbonate and concentrating, the ethereal solution deposited hard crystals which melted at 106—107°, and consisted of tetrahydromethylcryptopine, $C_{22}H_{29}O_5N$ (896). The latter is the principal product of the reduction of cryptopine methochloride under the conditions described at the beginning of this section. Experiments were also made on the reduction of cryptopine methosulphate (880) in alkaline solution with sodium amalgam, but the only product that could be isolated was tetrahydromethylcryptopine.

Section III (a).   *The Reduction of* isoCryptopine Chloride,

$$
\begin{array}{c}
\text{CH} \quad \text{CH}_2 \\
\parallel \quad \quad | \\
\text{C--NMeCl} \quad in \; Alkaline \; Solution. \\
\quad \quad | \\
\quad \text{CH}_2 \\
\text{CH}_2
\end{array}
$$
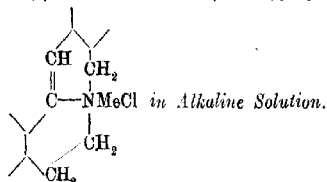
For the purpose of this investigation, crushed sodium amalgam (100 grams of 4 per cent.) was added to *iso*cryptopine chloride (5 grams), dissolved in about 400 c.c. of boiling water, and the whole placed on the steam-bath and well stirred, the water being replaced as it evaporated.

A viscid base soon began to separate, and, after an hour, the whole was filtered hot and the residue washed with hot water. The filtrate, mixed with excess of hydrochloric acid, deposited a large quantity of a quaternary salt, which was readily recognised as *iso*dihydrocryptopine β-chloride (compare p. 721), and this substance is produced in such considerable amount that this process affords a much more convenient means for its preparation than that previously described (934). The viscid base was dissolved in alcohol and mixed with much ether, which caused a further small quantity of the quaternary salt to separate; this was filtered off, the ethereal solution washed thoroughly until free from alcohol, quickly dried over potassium carbonate, and filtered. During the subsequent concentration, a base began to separate on the sides of the flask as a glistening, crystalline crust, and, on long keeping in the ice-chest, this increased considerably. When this deposit was fractionally crystallised from methyl alcohol, it separated into (i) considerable quantities of *tetrahydroanhydro*isocryptopine, $C_{21}H_{25}O_4N$ (m. p. 138°), identical with the base obtained as one of the products of the reduction of *iso*cryptopine chloride in acid solution (p. 751), and quite small quantities of a new base, $C_{21}H_{23}O_4N$—*dihydroanhydro*isocryptopine—melting at 195°, the constitution of which is represented by the formula

$$
\begin{array}{c}
\text{CH} \quad \text{Me} \\
\parallel \\
\text{CH--NMe} \\
\quad \quad | \\
\quad \text{CH}_2 \\
\text{CH}_2
\end{array}
$$
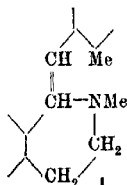
0·0829 gave 0·2174 CO_2 and 0·0480 H_2O. C=71·5; H=6·4.

0·1246 „ 0·3261 CO_2 „ 0·0729 H_2O. C=71·4; H=6·5.

$C_{21}H_{23}O_4N$ requires C=71·4; H=6·5 per cent.

This interesting substance separates from alcohol or methyl alcohol, in both of which it is very sparingly soluble, in pale lemon-yellow needles.

It is also sparingly soluble in boiling benzene or acetone, and separates particularly well from the latter in glistening needles. The solution in glacial acetic acid gives no coloration with sulphuric acid but, on the addition of a drop of dilute nitric acid, an intense permanganate coloration rapidly develops.

The Hydrochloride.—The base dissolves readily in dilute hydrochloric acid, and, on rubbing, the hydrochloride soon separates in needles. It is readily soluble in boiling water, but almost insoluble in dilute hydrochloric acid in the cold:

0·1151 gave 0·2721 CO_2 and 0·0652 H_2O. C=64·5; H=6·3.

$C_{21}H_{23}O_4N,HCl$ requires C=74·7; H=6·2 per cent.

The sulphate is soluble and does not appear to crystallise readily, but the addition of nitric acid to the dilute solution of the sulphate immediately precipitates the nitrate, which is very sparingly soluble in hot dilute nitric acid and crystallises rather indefinitely. When boiling dilute potassium iodide is added to the boiling dilute solution of the sulphate, a milky liquid is produced, from which the *hydriodide* soon separates as a crystalline mass. This was collected and recrystallised from boiling alcohol, in which the salt is sparingly soluble and from which it separates in warty aggregates melting at about 250—255° with decomposition to a yellow froth:

0·1046 gave 0·2017 CO_2 and 0·0471 H_2O. C=52·6; H=5·0.

$C_{21}H_{23}O_4N,HI$ requires C=52·4; H=5·0 per cent.

Section III (b). The Reduction of isoCryptopine Chloride in Acid Solution.

In attempting this reduction, considerable difficulty was experienced owing to the sparing solubility of *iso*cryptopine chloride in dilute hydrochloric acid, and, indeed, in mineral acids in general.

Ultimately, however, the following process was found to work well.

*iso*Cryptopine chloride (5 grams), dissolved in glacial acetic acid (25 c.c.), is mixed with boiling water (100 c.c.), and, after heating to boiling, concentrated hydrochloric acid (20 c.c.) is added, and the whole poured on sodium amalgam (100 grams of 4 per

cent.) in an enamelled iron basin. So soon as the vigorous action has subsided, the same quantity of sodium amalgam is again added, as well as sufficient hydrochloric acid to keep the liquid strongly acid. The whole while hot is decanted from the mercury on to a Büchner funnel connected with the pump, and the filtrate, which immediately begins to crystallise in minute needles, left overnight.

The precipitate (A) is collected, washed with a little water, the filtrate heated to boiling and mixed with excess of ammonia, when a viscid, grey mass (B) separates, which is immediately filtered off, and the filtrate, on keeping overnight, becomes filled with a soft mass of needles (C). The substance (A), which is almost pure *iso*cryptopine chloride, is again reduced as before, and, even after the operation has been repeated four times, *iso*cryptopine chloride still remains.

This was proved by analysis (Found: $C = 59\cdot3$; $H = 6\cdot3$. $C_{21}H_{22}O_4NCl,2H_2O$ requires $C = 59\cdot5$; $H = 6\cdot1$ per cent.) and also by the fact that the salt yielded anhydrocryptopine (975) on decomposition with methyl-alcoholic potassium hydroxide. The quaternary salt (C) crystallised well from hot dilute hydrochloric acid in long needles, and, in contact with porous porcelain, dried to a horny mass which did not melt at 260°. On examination, this salt was found to be *iso*dihydrocryptopine β-chloride, since, when digested with methyl-alcoholic potassium hydroxide, it yielded a substance which, after·crystallisation from acetone, melted at 178°, and was recognised as anhydrodihydrocryptopine (A) (938).

The viscid, grey mass (B) hardens on keeping, and becomes crystalline in contact with methyl alcohol. The whole is dissolved in boiling methyl alcohol and set aside, when a crop of crystals separates which usually consists of a mixture of *tetrahydroanhydro-isocryptopine* (m. p. 138°) and *dihydroanhydrodihydrocryptopine* (*A*) (m. p. 164°).

The latter of these is much the less soluble in methyl alcohol, and at some concentrations separates almost completely before the base, melting at 138°, begins to crystallise. If this is not the case, fractional crystallisation from methyl alcohol must be resorted to until separation is complete. The constitutional formulæ of the two bases and their derivatives are discussed fully in the intro-duction (pp. 722 and 723).

$$\text{Tetrahydroanhydroisocryptopine,}$$
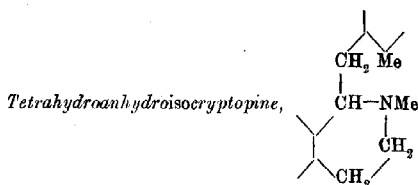
This base, obtained as described in the last section, separates from methyl alcohol in groups of striated, prismatic needles, and melts at 138—139°:

0·1139 gave 0·2958 CO_2 and 0·0731 H_2O. C = 70·8; H = 7·1.

0·1253 ,, 0·3264 CO_2 ,, 0·0804 H_2O. C = 71·0; H = 7·1.

$C_{21}H_{25}O_4N$ requires C = 71·0; H = 7·0 per cent.

Tetrahydroanhydroisocryptopine is readily soluble in boiling alcohol, acetone, or benzene, and crystallises well from all these solvents. Discoloured specimens of the base are readily purified by dissolving in dilute hydrochloric acid, digesting with animal charcoal, and precipitating with ammonia. In this condition, the base is soluble in ether, and. the ethereal solution, after drying over potassium carbonate and concentrating, deposits the base as a colourless, crystalline crust.

The *salts* with mineral acids are readily soluble, and crystallise from concentrated solutions in needles. Long boiling with concentrated hydrochloric acid does not appear to have any action on the hydrochloride, which separates, on keeping in the ice-chest, in balls of needles. The solution of a crystal of the base in acetic acid gives with sulphuric acid a pale brown coloration, which becomes greenish-brown on keeping, and the addition of a drop of dilute nitric acid changes the colour to deep port wine. The *platinichloride* is obtained, on the addition of platinic chloride to the dilute solution of the hydrochloride, as a pale yellow, caseous precipitate, which soon becomes crystalline. It dissolves appreciably in boiling water, and separates as a heavy, pale orange deposit consisting of groups of irregular plates:

0·1272 gave 0·2069 CO_2 and 0·0507 H_2O. C = 44·4; H = 4·5.

0·5064 ,, 0·0854 Pt. Pt = 16·9.

$(C_{21}H_{25}O_4N)_2,H_2PtCl_6$ requires C = 45·0; H = 4·6; N = 17·3 per cent.

The mercurichloride separates, on adding mercuric chloride to the dilute solution of the hydrochloride, as a white, caseous precipitate which soon becomes crystalline; it melts under boiling water, dissolves moderately readily, and, when cooled and rubbed, the milky liquid soon crystallises.

The Methosulphate.—This derivative is readily obtained by add-ing methyl sulphate (1 c.c.) to the solution of the base (1 gram) in warm benzene, when there is appreciable development of heat, but no immediate separation.* On keeping in the ice-chest, glistening plates soon begin to form, and, after twenty-four hours, the substance is collected and washed with benzene, but it was not recrystallised, because it is very readily soluble both in water and in methyl alcohol.

After drying in the steam-oven, it softened at 145° and melted at about 160° :

0·1185 gave 0·2509 CO_2 and 0·0686 H_2O.   C = 57·7; H = 6·4.

$C_{21}H_{25}O_4N,Me_2SO_4$ requires C = 57·4; H = 6·5 per cent.

The aqueous solution of this methosulphate gave no precipitate on the addition of ammonia or dilute sodium hydroxide.

The Methiodide.—The addition of hot dilute potassium iodide to the hot aqueous solution of the methosulphate produces a milky liquid, which soon crystallises beautifully in glistening scales:

0·1124 gave 0·2179 CO_2 and 0·0565 H_2O.   C = 52·7; H = 5·6.

$C_{21}H_{25}O_4N,MeI$ requires C = 53·1; H = 5·6 per cent.

This methiodide does not become yellow until about 250°, and melts at about 263°, without effervescence, to a lemon-yellow liquid. It is very sparingly soluble in water or alcohol, and separates, when the solution in the latter solvent is concentrated, as a glistening, heavy powder consisting of stout prisms with bevelled edges.

Anhydrotetrahydromethylcryptopine,
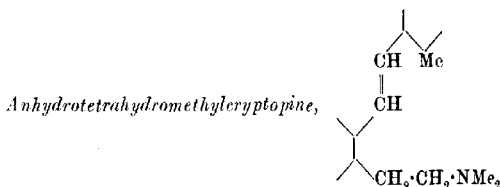
This substance is produced when the methosulphate of tetra-hydroanhydro*iso*cryptopine is decomposed by methyl-alcoholic potassium hydroxide. The methosulphate (1 gram) was boiled with methyl-alcoholic potassium hydroxide (10 c.c. of 20 per cent.) in an open flask for ten minutes, when decomposition set in readily and a cloudy liquid was produced, which soon deposited a white, crystalline precipitate. The product was mixed with water, heated

* If, however, the benzene solution is boiling, a vigorous reaction sets in, and the methosulphate commences to crystallise at once, the separation being complete in a few minutes.

to boiling, the aqueous liquid decanted from the viscid mass, and the latter recrystallised from methyl alcohol, from which it separated in glistening, colourless plates having a striking lilac fluorescence and melting at 107—109°. That this substance was anhydrotetrahydromethylcryptopine was proved by analysis (Found: $C=71\cdot2$; $H=7\cdot3$; $N=3\cdot9$. $C_{22}H_{27}O_4N$ requires $C=71\cdot5$; $H=7\cdot3$; $N=3\cdot8$ per cent.) and by the fact that a mixture of the substance with a specimen of anhydrotetrahydromethylcryptopine which had been prepared from tetrahydromethylcryptopine (899) melted at 106—108°. Moreover, a comparison of the crystals clearly established the identity of the two preparations.

Oxidation of Tetrahydroanhydroisocryptopine.—This oxidation, which has afforded valuable evidence in support of the constitution assigned to the above substance (p. 751), was carried out under the following conditions. The base (9 grams) was dissolved in warm acetone (400 c.c.), the solution cooled to the ordinary temperature, and then very finely powdered and sieved permanganate (13 grams) added in small quantities at a time with vigorous stirring. Oxidation was slow at first, but became more rapid as the temperature rose, and care was taken that the temperature remained below 20° throughout the operation. The product was filtered, the manganese precipitate thoroughly washed with acetone, and the acetone filtrate treated as described below.

When the manganese precipitate was extracted with boiling water, a very slightly coloured filtrate was obtained which, after concentrating considerably, yielded, on acidifying with hydrochloric acid, a very sparingly soluble, nearly colourless, chalky precipitate (2 grams). This was collected and crystallised from glacial acetic acid, from which it separated in needles melting at 215—216°, and yielded on analysis: $C=60\cdot0$; $H=4\cdot6$, whereas $C_9H_8O_4$ requires $C=60\cdot0$; $H=4\cdot5$ per cent. Careful comparison showed that this acid was identical with 5:6-methylenedioxy-*o*-toluic acid (916), $CH_2\!:\!O_2\!:\!C_6H_2Me\!\cdot\!CO_2H$.

The acetone solution, which had been filtered from the manganese precipitate as described above, was evaporated, when a yellow syrup remained, which gradually deposited needle-shaped crystals. When the whole was distilled in a current of steam, a milky distillate was obtained, which deposited a mass of crystals having the odour of piperonal, and, after recrystallisation from light petroleum, melted at 73—74°. That this substance was 5:6-methylenedioxy-*o*-tolualdehyde, $CH_2\!:\!O_2\!:\!C_6H_2Me\!\cdot\!CHO$, was proved by direct comparison with a specimen of this substance which had previously been obtained by the oxidation of anhydrotetrahydromethylcryptopine (907). The residue in the steam dis-

F F*

tillation flask was extracted with ether, the ethereal solution washed
with very dilute hydrochloric acid to remove any basic substances,
dried over potassium carbonate, and evaporated. When the resi-
dual, pale yellow syrup was seeded with a trace of 1-keto-6 : 7-
dimethoxy-2-methyltetrahydro*iso*quinoline,
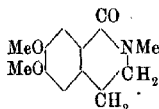
(m. p. 126°) (Pyman, T., 1909, **95**, 1272; 1910, **97**, 269), it rapidly
became crystalline. After remaining in contact with porous porce-
lain for a couple of days, the colourless, crystalline residue was
recrystallised from dry ether, from which it separated in prisms
melting at 126°. Moreover, the intimate mixture with a specimen,
prepared by the method described by Pyman, melted at the same
temperature.

Dihydroanhydrodihydrocryptopine (*A*),
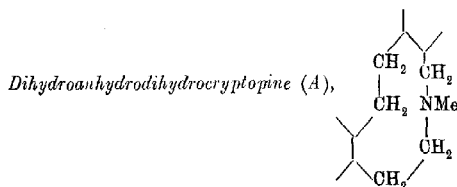
This base, produced by the reduction of *iso*cryptopine chloride
under the conditions specified on p. 750, separates from acetone
in which it is rather sparingly soluble, in groups of glistening
prisms, and melts at 163—164° :

0·1057 gave 0·2752 CO_2 and 0·0670 H_2O. $C = 71·0$; $H = 7·0$.
0·1036   ,,   0·2701 CO_2 ,,   0·0661 H_2O. $C = 71·1$; $H = 7·1$.
$C_{21}H_{25}O_4N$ requires $C = 71·0$; $H = 7·0$ per cent.

Dihydroanhydrodihydrocryptopine (*A*) is characterised by being
remarkably sparingly soluble in boiling methyl alcohol, from which
it separates in stars of flat needles; it is much more readily soluble
in ethyl alcohol, and readily so in benzene. The solution of a
crystal in a drop of acetic acid yields, on mixing with sulphuric
acid, at first no coloration, but gradually an intense indigo
develops, and the addition of a drop of dilute nitric acid changes
this to orange.

The *salts* of dihydroanhydrodihydrocryptopine (*A*) are much less
readily soluble in water or dilute acids than those of the isomeric

tetrahydroanhydro*iso*cryptopine (p. 751).   When dilute hydro-
chloric acid is added to the base, the crystals at first dissolve, but
almost at once the hydrochloride commences to separate, and is
very sparingly soluble in cold dilute hydrochloric acid.   It dissolves
readily, however, on boiling, and separates in groups of flat needles.
The sulphate is also sparingly soluble in dilute sulphuric acid, and
crystallises in long hairs radiating from a centre.   The base does
not dissolve in dilute nitric acid, but is at once converted into the
crystalline nitrate, which is more sparingly soluble than either the
hydrochloride or sulphate, and separates from its solution in hot
dilute nitric acid in stout, prismatic needles with bevelled edges.
When boiling dilute solutions of the hydrochloride and potassium
iodide are mixed, a clear solution is formed, from which the hydr-
iodide separates in stars of thin laminæ, and is almost insoluble in
cold water.   The *platinichloride* separates, on the addition of
platinic chloride to a hot dilute solution of the hydrochloride, as
a viscid, pale ochreous precipitate, which soon hardens; it is some-
what soluble in boiling water and crystallises in microscopic balls
of needles :

0·1130 gave 0·1848 CO_2 and 0·0464 H_2O.   C = 44·6; H = 4·6.
0·5052 ,,   0·0859 Pt.   Pt = 17·0.
$(C_{21}H_{25}O_4N)_2,H_2PtCl_6$ requires C = 45·0; H = 4·6; Pt = 17·3 per cent.

The addition of mercuric chloride to the dilute solution of the
hydrochloride produces a curdy precipitate resembling silver
chloride; this is somewhat soluble in boiling water and separates in
stars of prisms.

The picrate is a chrome-yellow precipitate which melts under boil-
ing water and dissolves with difficulty.

The Methosulphate.—When methyl sulphate (1 c.c.) is added to
the solution of the base (1 gram) in benzene (10 c.c.), there is no
separation at first, but, in a minute or two, the liquid clouds and a
viscid syrup is deposited which crystallises on rubbing, the whole
becoming a glutinous mass of soft needles.   The substance is rather
difficult to collect, and is so readily soluble in water or methyl
alcohol that it could not be recrystallised.   After drying in the
steam-oven, it yielded the following analysis :

0·1191 gave 0·2499 CO_2 and 0·0701 H_2O.   C = 57·2; H = 6·6.
$C_{21}H_{25}O_4N,Me_2SO_4$ requires C = 57·4; H = 6·5 per cent.

The aqueous solution of this methosulphate gives no precipitate
on the addition of ammonia, and a trace of the salt, dissolved in
glacial acetic acid, gives no characteristic coloration on the addition
of sulphuric acid.

It is mentioned in the introduction (p. 723) that dihydroanhydro-

v v* 2

dihydrocryptopine (A) is unusually resistant towards perman-
ganate, and this was evidenced by the following experiment. A
few milligrams of very finely powdered permanganate were added
to the solution of the base (3 grams) in acetone (150 c.c.), but no
appreciable oxidation had taken place after remaining at 0° for
fifteen minutes. When the temperature was raised to 20°, oxida-
tion took place more rapidly, and, after 5 grams of permanganate
had been reduced, the product, worked up in the usual manner,
yielded 0·175 gram of unchanged base. A small quantity of a
resinous, sparingly soluble acid was produced, and also an oily
base, but the quantities of these were quite insufficient for further
investigation.

Reduction of Anhydrodihydrocryptopine (A, 938) *to Dihydro-
anhydrodihydrocryptopine* (A).—This conversion, which affords
welcome confirmation of the constitution assigned to the last-named
substance (p. 723), was carried out under the following conditions:
Anhydrodihydrocryptopine (A) (m. p. 178°; 7 grams), dissolved in
boiling water and concentrated hydrochloric acid (50 c.c.), was
poured on freshly prepared 4 per cent. sodium amalgam (350
grams) in an enamelled iron basin, and the whole well stirred until
the amalgam had been completely used. The product contained
a colourless, satiny mass of needles, and enough boiling water was
added to bring the whole into solution. After filtering, excess of
ammonia was added, when a caseous mass separated, which was
washed with a little cold water and digested with boiling water
to dissolve out a quaternary salt which was present (see below).
The residue was dissolved in boiling methyl alcohol, when, on
keeping, glistening crystals separated which melted at 162—163°,
and consisted of dihydroanhydrodihydrocryptopine (A), since the
admixture with a specimen of this substance which had been pre-
pared by the method described at the commencement of this section
melted at 162—164°. The identity was confirmed by analysis.
The aqueous ammoniacal filtrate from the base (A) deposited,
on keeping, a considerable crop of a quaternary salt as
a satiny mass of needles. This was collected and identified as
*iso*dihydrocryptopine β-chloride (934), since it did not melt at
260°, and, when digested with methyl-alcoholic potassium hydr-
oxide, yielded anhydrodihydrocryptopine (A), melting at 178°.

Dihydroisoanhydrodihydromethylcryptopine,

$$\begin{array}{c} \text{CH}_2 \ \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \ \text{NMe}_2 \end{array}$$

$$\text{CH:CH}_2$$
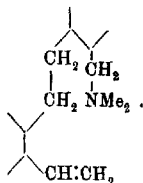
This beautiful substance is obtained when the methosulphate of dihydroanhydrodihydrocryptopine (A) is digested with methyl-alcoholic potassium hydroxide. The methosulphate (3 grams) was dissolved in hot methyl alcohol (25 c.c.), mixed with methyl-alcoholic potassium hydroxide (20 c.c. of 20 per cent.), and heated to boiling in an open flask in such a way that there was consider-able concentration. The decomposition took place rather slowly, and, after fifteen minutes, the cloudy solution was mixed with water, when a gum separated which showed no signs of crystallisation on rubbing with methyl alcohol. The whole was extracted with pure ether, the ethereal solution carefully washed, dried over potassium carbonate, concentrated, and left in the ice-chest in a corked flask. For some days nothing separated, and then gradually splendid hard, colourless, brilliant prisms began to form, and increased considerably during three weeks:

0·1106 gave 0·2890 CO_2 and 0·0730 H_2O. C = 71·2; H = 7·3.
0·1215 „ 0·3191 CO_2 „ 0·0803 H_2O. C = 71·5; H = 7·4.
$C_{22}H_{27}O_4N$ requires C = 71·5; H = 7·3 per cent.

Dihydroisoanhydrodihydromethylcryptopine melts at 75—77°, and is very readily soluble in the usual solvents. The crystals have been examined by Miss M. W. Porter, with the following results:

FIG. 2.
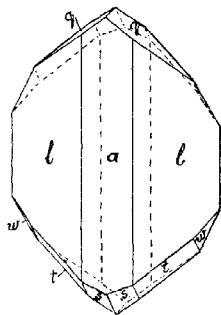
Dihydroisoanhydrodihydromethylcryptopine.

The substance is monoclinic with axial ratios $a:b:c=0\cdot6657:1:$ $0\cdot6899$, $\beta=99°34'$. The forms observed are: $a(100)$, $l(210)$, $q(011)$, $s(\bar{2}12)$, $t(\bar{2}32)$, $w(\bar{1}21)$, and, very rarely, $b(010)$, which accordingly is not shown in Fig. 2. Three crystals were measured on the two-circle goniometer, and the mean measured and calculated results are given below:

Face.	No. of readings.	φ (Azimuth).		ρ (Polar distance).	
		Obs.	Calc.	Obs.	Calc.
a (100)	6	90° 9′	90° 0′	90° 0′	90° 0′
b (010)	1	359 29	0 · 0	90 0	90 0
l (210)	7	*71 50	—	90 0	90 0
q (011)	3	*13 43	—	*35 23	—
s ($\bar{2}12$)	2	292 0	291 32	42 57	42 13
t ($\bar{2}32$)	6	320 1	319 49	53 10	53 33
w ($\bar{1}21$)	4	329 10	327 39	58 47	58 31

The salts of this base are very readily soluble in water and show little tendency to crystallise. The *platinichloride* was obtained as a pale salmon, chalky precipitate on adding platinic chloride to the dilute solution of the hydrochloride:

$0\cdot1171$ gave $0\cdot1981$ CO_2 and $0\cdot0518$ H_2O. $C=46\cdot2$; $H=4\cdot9$.
$0\cdot2028$ „ $0\cdot0339$ Pt. Pt$=16\cdot7$.
$(C_{22}H_{27}O_4N)_2,H_2PtCl_6$ requires $C=46\cdot0$; $H=4\cdot9$; Pt$=16\cdot9$ per cent.

The solution of a crystal of the base in glacial acetic acid gives, with sulphuric acid, a feeble brown coloration, and the addition of a drop of dilute nitric acid changes this to intense port wine. The methosulphate is obtained by adding methyl sulphate (1 c.c.) to the solution of the base (1 gram) in benzene (5 c.c.), when there is distinct rise of temperature and a syrup separates, which gradually crystallises, especially when triturated with ether. This substance is so readily soluble and so badly characterised that no attempt was made to purify it for the purpose of analysis. Its aqueous solution gives no precipitate on the addition of ammonia.

Dihydro-α-isocryptopidol (947),

$$CH_2 \quad CH_2\cdot OH$$
$$CH_2$$
$$CH:CH_2$$
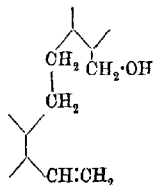
This unsatisfactory substance is obtained from the methosulphate of dihydro*iso*anhydrodihydromethylcryptopine by the action of methyl-alcoholic potassium hydroxide, trimethylamine being eliminated.

The methosulphate (3 grams), dissolved in a little methyl alcohol, was digested with methyl-alcoholic potassium hydroxide (30 c.c. of 25 per cent.) in an open flask heated just to boiling by means of a salt-solution bath for an hour, the temperature then being raised so that most of the methyl alcohol distilled away and there was no further development of trimethylamine. The residue was mixed with water, the viscid precipitate dissolved in methyl alcohol, mixed with much ether, and the ethereal solution washed with water until quite free from methyl alcohol. After drying over potassium carbonate and concentrating to a small bulk, nothing separated on keeping in the ice-chest for three weeks. The solution was therefore evaporated, when a colourless syrup remained which gradually crystallised, and the buttery mass was left in contact with porous porcelain until dry, but owing to the fact that the substance is so unusually readily soluble in the ordinary solvents and exhibits so little tendency to crystallise, no further purification was possible. After remaining over phosphoric oxide in a vacuum desiccator for a week, the following results were obtained on analysis :

0·1255 gave 0·3201 CO_2 and 0·0798 H_2O.   C = 69·6 ; H = 6·8.

$C_{20}H_{22}O_5$ requires C = 70·2 ; H = 6·4 per cent.

This result, coupled with its method of formation, clearly indicates that this substance is *dihydro-α-isocryptopidol*.

Section III (c).   Dihydroanhydrotetrahydromethylcryptopine,

$$\overset{|}{\diagup}\diagdown$$
$$\underset{|}{CH_2}\ Me$$
$$CH_2$$
$$\diagdown\diagup$$
$$\overset{|}{\diagdown}CH_2 \cdot CH_2 \cdot NMe_2$$
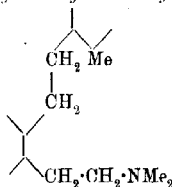
As explained on p. 725, this substance is obtained when the methosulphate either of tetrahydroanhydro*iso*cryptopine (m. p. 138°, p. 752) or dihydroanhydrodihydrocryptopine (*A*) (m. p. 164°, p. 755) is reduced in alkaline solution by sodium amalgam.

(i) *Reduction of the Methosulphate of Tetrahydroanhydroiso-cryptopine.*

The solution of this substance (3 grams) in hot water (150 c.c.) is reduced only with considerable difficulty by sodium amalgam (150 grams of 3 per cent.) even on the steam-bath, but a colour-

less oil gradually separates. After the action had proceeded for two hours, the product was left in the ice-chest, when the oil solidified. The mass was well washed and dissolved in hot dilute hydrochloric acid, when, on cooling to 0° and rubbing, the hydrochloride separated as a voluminous mass of needles. This salt, which is very sparingly soluble in dilute hydrochloric acid, but readily so in water, was collected, washed with dilute hydrochloric acid, the cold aqueous solution mixed with ammonia, and the milky liquid extracted with ether.   The ethereal solution, dried over potassium carbonate and concentrated, did not yield any crystals on remaining in the ice-chest for a week, but on evaporating off the ether, the residual, colourless syrup suddenly crystallised in balls of needles. After leaving in contact with porous porcelain until traces of oily impurity had been absorbed, the colourless, crystalline residue was dissolved in methyl alcohol, in which it is very readily soluble, and the solution allowed to concentrate nearly to dryness over sulphuric acid in a vacuum desiccator. The mass of plates which separated was drained on porous porcelain and recrystallised from a very small quantity of light petroleum, in which the base is very readily soluble.

(ii) *Reduction of the Methosulphate of Dihydroanhydrodihydro-cryptopine (A)*.

This process was carried out exactly as described under (i), when it was noticed that in the present case the oily base began to separate the moment the hot aqueous solution of the methosulphate was poured on the crushed sodium amalgam.   The method of extraction and purification were the same as those described under (i).

The careful examination of the bases obtained from (i) and (ii) showed that both consisted of *dihydroanhydrotetrahydromethyl-cryptopine*, since both preparations melted at 60—63°, and the mixture also melted at this temperature. The two analyses were made with specimens prepared according to (i) and (ii) respectively:

(i) 0·1126 gave 0·2935 CO_2 and 0·0798 H_2O. C = 71·1; H = 7·9.
(ii) 0·1185 „ 0·3077 CO_2 „ 0·0813 H_2O. C = 70·9; H = 7·9.

$C_{22}H_{29}O_4N$ requires C = 71·1; H = 7·8 per cent.

This base is characterised by its ready solubility in the usual organic solvents; the salts are readily soluble in water, but sparingly so in dilute acids, and generally crystallise well.

The *hydrochloride*, described above, is almost insoluble in cold dilute hydrochloric acid, and melts at 213°. It is very readily

soluble in warm glacial acetic acid, and also in boiling methyl alcohol, and separates from the latter in groups of needles. The addition of potassium iodide to the boiling methyl-alcoholic solution of the hydrochloride gives a clear liquid, from which the hydriodide separates in stars of needles. It is comparatively readily soluble in boiling methyl alcohol, crystallises well, and melts at about 212°. The nitrate separates from dilute nitric acid, in which it is very sparingly soluble, as a felted mass of long hairs. The solution of a crystal of the base in a drop of acetic acid gives scarcely any coloration with concentrated sulphuric acid, but the addition of a drop of dilute nitric acid produces an intense brown, changing to deep cherry-red.

Dihydroanhydrotetrahydromethylcryptopine Methosulphate,
$C_{22}H_{29}O_4N,Me_2SO_4$.

This well-characterised derivative separates in needles when the solution of the base (2 grams) in benzene (20 c.c.) is mixed with methyl sulphate (2 c.c.). It was collected, washed with benzene, and dried in the steam-oven, when the glistening crystals became opaque and chalky:

0·1210 gave 0·2577 CO_2 and 0·0747 H_2O. C=58·0; H=6·9.
$C_{22}H_{29}O_4N,Me_2SO_4$ requires C=57·9; H=7·0 per cent.

This methosulphate melts at 165—167°, without evolution of gas, to a colourless syrup, and is readily soluble in methyl alcohol or water.

The boiling aqueous solution gives, on the addition of potassium bromide, a milky liquid, from which the methobromide gradually separates in long, well-developed, four-sided, prismatic needles with flat ends.

The *methiodide* is obtained by adding boiling dilute potassium iodide to the boiling dilute aqueous solution of the methosulphate, when the clear solution, on rubbing, deposits tufts of needles:

0·1158 gave 0·2286 CO_2 and 0·0657 H_2O. C=53·8; H=6·2.
$C_{22}H_{29}O_4N,MeI$ requires C=53·8; H=6·2 per cent.

The dry substance is a satiny mass which darkens at about 230° and melts at about 240° with very little decomposition.
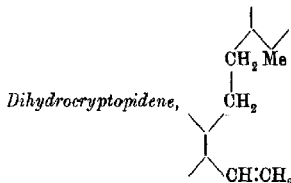
$$\textit{Dihydrocryptopidene,} \qquad \begin{array}{c} | \\ \diagup \diagdown \diagup \\ \mathrm{CH_2\ Me} \\ | \\ \mathrm{CH_2} \\ \diagup \diagdown \\ | \\ \diagup \diagdown \mathrm{CH:CH_2} \end{array}$$

This fine substance is obtained when the methosulphate of dihydroanhydrotetrahydromethylcryptopine is decomposed by methyl-alcoholic potassium hydroxide. The methosulphate (1 gram) dissolves readily in warm methyl-alcoholic potassium hydroxide (10 c.c. of 20 per cent.), and trimethylamine is readily eliminated. After boiling for fifteen minutes, the bulk of the methyl alcohol was distilled off, during which the liquid clouded, and, on adding water, a milky liquid was obtained, which was extracted with much ether. The ethereal solution was thoroughly washed, dried over anhydrous potassium carbonate, and rapidly filtered, when the new substance began to separate immediately as a voluminous mass of soft needles, and a further quantity was obtained from the concentrated ethereal solution. For analysis, the substance was recrystallised from ether:

0·1083 gave 0·2932 CO_2 and 0·0673 H_2O.   C=73·8; H=6·9.
$C_{20}H_{22}O_4$ requires C=73·6; H=6·7 per cent.

Dihydrocryptopidene melts at 126—128°, or almost at the same temperature as cryptopidene (m. p. 124°; compare 926), but the mixture of the two substances softens at 105° and is almost completely melted at 108°, so that there can be no question of identity. Moreover, the ethereal solution of dihydrocryptopidene exhibits to only a very slight degree the beautiful lilac fluorescence so characteristic of cryptopidene. Dihydrocryptopidene is unusually sparingly soluble even in boiling methyl alcohol, and separates as a voluminous, woolly mass of needles which fill the entire liquid. The solution of the substance in acetic acid is coloured at first pale brown and then deep cherry-red by sulphuric acid, and a drop of dilute nitric acid changes the colour to intense brown.

Ketodihydrocryptopidene (I) *and Dihydrocryptopidenic Acid* (II),

$$
\begin{array}{ccc}
\text{CO} \quad \text{Me} & & \text{CH}_2 \quad \text{Me} \\
| & & | \\
\text{CH}_2 & \text{and} & \text{CH}_2 \\
& & \\
\diagdown\diagup & & \diagdown\diagup \\
\diagup \text{CH:CH}_2 & & \diagup \text{CO}_2\text{H} \\
(\text{I.}) & & (\text{II.})
\end{array}
$$
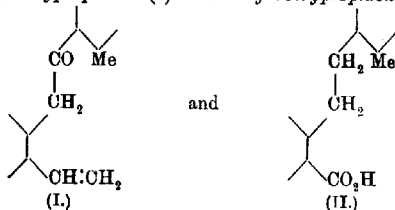
These interesting substances are produced when dihydrocryptopidene is oxidised in acetone solution with permanganate. The substance (2 grams), dissolved in acetone (150 c.c.), was gradually mixed with finely divided permanganate (3 grams) at the ordinary temperature, when, contrary to expectation, oxidation took place rapidly and with the development of so much heat that cooling was necessary in order to keep the temperature below 15°. The product was filtered, the manganese precipitate (A) washed thoroughly with acetone, and the acetone distilled off, when an almost colourless syrup (0·9 gram) remained, which immediately commenced to crystallise, and crystallisation was much hastened by triturating with methyl alcohol. The product was several times recrystallised from methyl alcohol in order to remove traces of unoxidised dihydrocryptopidene:

0·1151 gave 0·2987 CO_2 and 0·0647 H_2O.   C = 70·8; H = 6·2.

$C_{20}H_{20}O_5$ requires C = 70·6; H = 5·9 per cent.

Ketodihydrocryptopidene melts at about 116°, but this melting point is probably not quite accurate, owing to the difficulty of removing the last traces of dihydrocryptopidene. It is characterised by the intense purple coloration which a trace, dissolved in a drop of acetic acid, yields on mixing with much sulphuric acid, and this colour changes to brown on the addition of a drop of dilute nitric acid. When concentrated nitric acid is poured on a trace of the substance rubbed on a watch-glass, a blue solution is produced, and, on warming, a dark green mass separates. Ketodihydrocryptopidene does not yield an acetyl derivative when it is boiled with acetic anhydride and anhydrous sodium acetate, since the unchanged substance separates on the addition of water.

The Semicarbazone.—This derivative was prepared by boiling the alcoholic solution of crude dihydrocryptopidene (as directly obtained from the oxidation of dihydrocryptopidene) with a large excess of a concentrated aqueous solution of semicarbazide acetate for an hour.

On the addition of water, a caseous mass was precipitated, which was separated into the semicarbazone and dihydrocryptopidene by recrystallisation from methyl alcohol. The semicarbazone is sparingly soluble in methyl alcohol, and crystallises as a voluminous mass of needles melting at about 185—190°:

0·1509 gave 13·2 c.c. N_2 at 12° and 766 mm. $N = 10·2$.
    $C_{21}H_{23}O_5N_3$ requires $N = 10·6$ per cent.

Dihydrocryptopidenic Acid.—The manganese precipitate (A, see above) from the oxidation of dihydrocryptopidene was extracted with boiling water, the brown extract boiled with animal charcoal, and acidified, when a viscid acid separated, which gradually hardened and immediately became crystalline on rubbing with glacial acetic acid. This was collected, drained on porous porcelain, and dissolved in boiling glacial acetic acid, from which the new acid separated in long, prismatic needles.

The recrystallised acid yielded the following analytical results:

0·1045 gave 0·2522 CO_2 and 0·0572 H_2O. $C = 65·8$; $H = 6·1$.
0·1142 ,,   0·2777 CO_2 ,, 0·0627 H_2O. $C = 66·2$; $H = 6·1$.
    $C_{19}H_{20}O_6$ requires $C = 66·3$; $H = 5·8$ per cent.

Dihydrocryptopidenic acid melts at 194—195°, and is sparingly soluble in cold methyl alcohol, but dissolves more readily on boiling, and crystallises in stars of slender needles; it is almost insoluble in cold water. The solution in glacial acetic acid gives, with sulphuric acid, an olive-brown coloration, which becomes redder on the addition of a drop of dilute nitric acid. When concentrated sulphuric acid is poured on a trace of the acid rubbed on a watch-glass, an intense green colour is produced, which soon changes to purplish-brown, and a green precipitate separates on the addition of water. Concentrated nitric acid does not give a colour reaction with the acid.

The sodium and potassium salts of the acid are readily soluble and give with hydrochloric acid a gelatinous precipitate, which only very gradually becomes crystalline. The titration with $N/10$-sodium hydroxide did not give very accurate results, owing to the uncertainty of the end-point. In one experiment, 0·308 neutralised 0·0385 NaOH, whereas this amount of a monobasic acid, $C_{19}H_{20}O_6$, should neutralise 0·0359 NaOH.

The Anilide, $C_{18}H_{19}O_4 \cdot CO \cdot NH \cdot C_6H_5$.—This derivative was prepared mainly with the object of controlling the composition of the acid. The acid was warmed with excess of freshly distilled phosphorus trichloride at 60—70°, when it dissolved completely and with very little discoloration. The excess of the trichloride was then distilled off under reduced pressure and the residue mixed

with much dry ether and excess of aniline. The ethereal solution was washed with very dilute hydrochloric acid, then with water, and the ether evaporated, when a crystalline residue was obtained which was digested with dilute ammonia in order to remove any traces of unchanged acid. Finally, the anilide was recrystallised from glacial acetic acid, from which it separated in glistening needles melting at about 185°:

0·1128 gave 0·2953 CO_2 and 0·0597 H_2O. $C = 71\cdot4$; $H = 5\cdot9$.

$C_{25}H_{25}O_5N$ requires $C = 71\cdot6$; $H = 6\cdot0$ per cent.

Section IV.

The Quaternary Salts of ψ-Cryptopine.

During the course of this investigation, it has been necessary on several occasions to make a close comparison of certain quaternary salts, thought to be new, with the corresponding quaternary salts of ψ-cryptopine, and this has necessitated a more accurate characterisation of the latter than had been made in Part I. of this research (984).

The following is a brief account of the principal properties of these interesting salts.

ψ-Cryptopine Chloride,
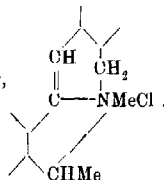
The formation of this salt from anhydrocryptopine methosulphate by boiling with concentrated hydrochloric acid has already been described (984), but the method of preparation there recommended may be simplified in the following manner. Anhydrocryptopine methosulphate (10 grams) is mixed in a small flask with concentrated hydrochloric acid (20 c.c.), gently warmed until solution is complete, and the whole boiled for five minutes in such a way that about a third of the hydrochloric acid escapes; the pale brown syrup is then mixed with two volumes of boiling water. On remaining in the ice-chest, the liquid becomes filled with needles of ψ-cryptopine chloride, which is collected, washed with dilute hydrochloric acid, and recrystallised from this solvent. The yield is about 60 per cent. of that theoretically possible, and a further small quantity may be obtained by allowing the brown mother

liquor to concentrate over solid potassium hydroxide in a vacuum desiccator. The remaining mother liquor contains a considerable quantity of quaternary salt, the nature of which has not been established. When ψ-cryptopine chloride is dried at 100° until it has lost its water of crystallisation, the residue is much discoloured and sometimes brick-red; there was therefore a possibility that the original analysis of the anhydrous chloride was untrustworthy. Further analyses leave, however, no doubt that the chloride has the formula $C_{21}H_{22}O_4NCl$ originally assigned to it, and this is confirmed by the analyses of the iodide, $C_{21}H_{22}O_4NI$, the bromide, $C_{21}H_{22}O_4NBr$, and the platinichloride,

$$(C_{21}H_{22}O_4N)_2PtCl_6.$$

In order to determine the actual composition of the crystallised chloride, two specimens were repeatedly crystallised from dilute hydrochloric acid and left on watch-glasses in the dark until the weight was constant. The substance melted at 117—120° with evolution of steam, solidified again, and then melted at about 150—152°, with evolution of gas, to an orange-red froth. The determination of the water of crystallisation was made by drying in the steam-oven in the case of (a) and (b), and the analysis (c) was done with substance which had been dried over phosphoric oxide in a vacuum desiccator, when the whole of the water was thereby removed with scarcely any discoloration:

(a) 0·1389 lost 0·0290. $H_2O = 20\cdot9$.

(b) 0·8106 „   0·1628. $H_2O = 21\cdot1$.

(c) 0·1099 gave 0·2611 CO_2 and 0·0593 H_2O. $C = 64\cdot6$; $H = 6\cdot0$.

$C_{21}H_{22}O_4NCl,6H_2O$ contains $H_2O = 21\cdot7$ per cent.

$C_{21}H_{22}O_4NCl$ requires $C = 65\cdot0$; $H = 5\cdot7$ per cent.

Dry ψ-cryptopine chloride crystallises from anhydrous methyl alcohol, in which it is readily soluble, in clusters of needles which, when heated at 100°, become opaque, and the anhydrous residue darkens at 190°, is very dark at 205°, and melts at 210° with effervescence to a black froth:

0·1048 gave 0·2498 CO_2 and 0·0556 H_2O. $C = 65\cdot0$; $H = 5\cdot9$.

$C_{21}H_{22}O_4NCl$ requires $C = 65\cdot0$; $H = 5\cdot7$ per cent.

In addition to the remarkable colour changes already recorded (985), it may be mentioned that the solution of ψ-cryptopine chloride in dilute sulphuric acid gives a reddish-violet on dusting in finely divided manganese dioxide, and an intense cherry-red develops on boiling.

A series of experiments on the action of dilute hydrochloric acid on anhydrocryptopine methosulphate was made with the object of determining whether this substance would behave towards dilute

acids in a manner similar to that which leads, under these conditions, to the formation of the hydroxy*iso*anhydrodihydrocryptopines from anhydrocryptopine itself (994).

The unexpected result was, however, obtained that, even when boiled with dilute hydrochloric acid, anhydrocryptopine methosulphate loses an N-methyl group and yields ψ-cryptopine chloride. Thus the methosulphate (2 grams), heated on the steam-bath for forty minutes with concentrated hydrochloric acid (2 c.c.) and water (5 c.c.), gives a deep yellow solution. On keeping in the icechest, this deposits a mass of needles which, on examination and analysis, proved to be ψ-cryptopine chloride.

ψ-*Cryptopine Bromide*, $C_{21}H_{22}O_4NBr$.—In preparing this characteristic salt, carefully purified ψ-cryptopine chloride, dissolved in boiling water, was mixed with a large excess of boiling potassium bromide, when a clear solution resulted, from which microscopic needles soon separated. The bromide was collected, recrystallised from dilute potassium bromide, and then once from water. The air-dry salt contains apparently $5H_2O$, all of which is lost at 95°:

0·1165, heated at 95°, lost 0·0204. $H_2O = 17·6$.

0·1165 gave 0·2476 CO_2 and 0·0533 H_2O. $C = 58·0$; $H = 5·1$.

$C_{21}H_{22}O_4NBr,5H_2O$ contains $H_2O = 17·2$, and $C_{21}H_{22}O_4NBr$
  requires $C = 58·3$ and $H = 5·1$ per cent.

This bromide exists in well-defined, dimorphic forms. The needles (A) from water, dried at 90°, melt with decomposition at about 130—135°; solidification then takes place, and the next melting point observed is about 230° with effervescence to a reddish-brown froth. When the anhydrous substance (A) is boiled with ethyl or methyl alcohol, it dissolves, and the solution now deposits well-developed prisms (B), which become opaque in the steam-oven.

The modification (B) melts at about 245° with vigorous effervescence to a reddish-brown froth, and crystallises particularly well from glacial acetic acid as a mass of glistening, sulphur-yellow prisms, which Mr. T. V. Barker has described as follows. The macroscopic crystals are strongly doubly refracting, stout, rectangular prisms with straight extinction. In convergent light, an optic axis nearly central. When crystallisation is rapid, there is a marked tendency to form lenticular crystals having diagonal extinction. The modification (A) becomes slate-coloured on exposure to light, and is comparatively readily soluble in boiling water, yielding a nearly colourless solution which gelatinises on rapid cooling. Modification (B) is sparingly soluble in hot water, and becomes deep salmon on exposure to light. Both modifications

give the remarkable colour reactions which have been described in detail in the case of the corresponding chloride (985).

ψ-*Cryptopine Iodide*, $C_{21}H_{22}O_4NI$.—This substance has been described (984) as a glistening mass of scales melting at 232—235°.

During the preparation of larger quantities, it was observed that this iodide exists in dimorphic modifications (*A*) and (*B*), melting at 225—227° and 240—242° respectively. When a hot solution of ψ-cryptopine chloride is mixed with hot dilute potassium iodide, a heavy, crystalline precipitate separates, which becomes brick-red at 220°, melts at 232—235°, and consists of modification (*A*). It may be recrystallised from methyl alcohol, if the operation is rapidly carried out, and is obtained in flat, prismatic needles. When, however, it is boiled for a considerable time with methyl alcohol insufficient completely to dissolve it, the needles gradually give place to short, well-defined prisms which are exceedingly sparingly soluble even in boiling methyl alcohol, melt at 240—242°, and consist of modification (*B*). This modification is also sparingly soluble in boiling glacial acetic acid, and separates in iridescent, yellow scales resembling lead iodide, and these, under the microscope, are seen to consist of flat prisms with truncated ends.

ψ-*Cryptopine Hydrogen Sulphate*, $C_{21}H_{22}O_4N,HSO_4$.—This quaternary salt is obtained when anhydrocryptopine methosulphate (5 grams), dissolved in water (13 c.c.) and sulphuric acid (2 c.c.), is heated for two hours on the steam-bath. On remaining in the ice-chest, the deep yellow solution deposits a crystalline mass which, under the microscope, is seen to consist of warts and to be quite homogeneous.

This was collected, recrystallised from dilute sulphuric acid, in which it is rather sparingly soluble, washed twice with a little water, and drained on porous porcelain. It was then recrystallised from a little water and dried in the steam-oven :

0·1116 gave 0·2315 CO_2 and 0·0530 H_2O.   C = 56·5 ; H = 5·3.

$C_{21}H_{22}O_4N,HSO_4$ requires C = 56·1 ; H = 5·1 per cent.

ψ-*Cryptopine hydrogen sulphate* becomes yellow at 180°, deep yellow at 200°, and decomposes at about 215—220° to an orange-red froth.

It exhibits in a very striking manner the characteristic colour reactions described in detail in the case of ψ-cryptopine chloride (985). The relationship of the sulphate to the latter is also evidenced by the fact that, on precipitation with potassium iodide, both yield the (*A*) and (*B*) modifications of ψ-cryptopine iodide (see above). A rather concentrated solution of the sulphate gives, on the addition of dilute nitric acid, an immediate chalky

precipitate of the nitrate; this dissolves on warming and separates in a highly characteristic manner, namely, as an iridescent mass which, under the microscope, is seen to consist of thin, lenticular or boat-shaped plates.

Section IV (a). *The Reduction of ψ-Cryptopine Chloride in Alkaline Solution : Formation of ψ-Anhydrodihydrocryptopine (A) (841),*
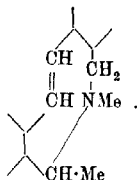
When ψ-cryptopine chloride (2 grams),* dissolved in water (100 c.c.) and rendered slightly alkaline by the addition of sodium hydroxide, is placed on crushed sodium amalgam (50 grams of 4 per cent.) and the whole heated on the steam-bath, a viscid base soon commences to separate, which gradually crystallises and ultimately becomes quite hard. When the separation was complete, the base was collected, thoroughly washed, dissolved in methyl alcohol, mixed with much ether, and the solution washed until free from methyl alcohol, during which a small quantity of a slimy, quaternary salt separated, which was not examined. After filtering and drying over potassium carbonate, the claret-coloured solution was concentrated considerably and left in the ice-chest, when a thick crust of pale brown prisms gradually separated, which were collected and washed with ether. The mother liquor was evaporated, and the residual purplish-brown syrup mixed with methyl alcohol and nucleated with a crystal from the first crop, when it immediately began to crystallise, and, after collecting and washing with a little methyl alcohol, a considerable pale brown, crystalline mass remained. The combined crops were recrystallised from methyl alcohol, from which the new substance separates splendidly in short, glistening needles growing to stout prisms :

0.1240 gave 0.3255 CO_2 and 0.0728 H_2O.   C = 71.5; H = 6.5.

$C_{21}H_{23}O_4N$ requires C = 71.4; H = 6.5 per cent.

* Not more than 2 grams should be employed and the experiment should be conducted as rapidly as possible, otherwise the product will be very dark coloured owing to the formation of a black base due to the action of the alkali on ψ-cryptopine chloride (985).

The prisms have been measured by Mr. T. V. Barker.

The platy crystals of this substance belong to the monoclinic system. Crystallographic constants: $21°3'$, $a(73°13')m(16°47')b$, $43°13'$, $74°18'$, or, alternatively, $a:b:c = 3·446:1:2·598$, $\beta = 105°42'$. The habit of the crystals is shown in Fig. 3, the observed forms being $a(100)$, $c(001)$, $r(\bar{1}01)$, $o'(\bar{1}11)$, and $o(111)$. Two crystals were measured on the two-circle goniometer, with the following results:

	$a(100)$.	$c(001)$.	$r(\bar{1}01)$.	$o'(\bar{1}11)$.	$o(111)$.
Azimuth	Face of	$90°\ 0'$	$90°\ 0'$	*$21°\ 3'$	$21°17'$ $(21°3')$
Polar distance	reference *74 18	*116 40	100 18 (100°14') 69 29	(69 4)	

Determinants: $121/1\bar{2}1/10\bar{1}$.   Complex-symbol: $3d$; $-1/69\frac{1}{2}/-9\frac{1}{2}$.

Optically, the extinction on $a(100)$ is parallel with the edge ac. In convergent light, a wide biaxial figure is visible through a, indicating the symmetry plane as plane of the optic axes.

FIG. 3.
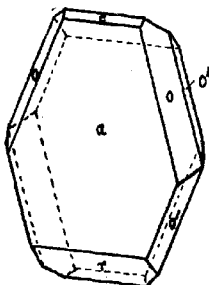
ψ-*Anhydrodihydrocryptopine* (A) melts at $112°$, and is very readily soluble in benzene, ether, or acetone, but sparingly so in light petroleum.

The solution of a trace in a drop of acetic acid gives, with sulphuric acid, a deep orange-red coloration, and the addition of a drop of dilute nitric acid changes this to crimson, which becomes more intense on warming. A trace rubbed on a watch-glass is coloured deep brown by concentrated nitric acid. The hydrochloride and sulphate of the base are readily soluble and exhibit little tendency to crystallise, but the nitrate is characteristic. This salt is obtained, when the base is rubbed with dilute nitric acid, as a crystalline mass very sparingly soluble in cold dilute nitric acid; it dissolves, however, on warming and separates in stars of long, thin plates. The sparing solubility and tendency to crystallise of

this salt have been made use of, with success, in purifying dark-coloured specimens of the crude base. The solution of the sulphate gives, on the addition of potassium iodide, a milky liquid, from which the iodide separates on rubbing, and crystallises from water, in which it is rather readily soluble, in six-sided prisms.

The *Methosulphate*, $C_{21}H_{23}O_4N,Me_2SO_4$.—The solution of ψ-anhydrodihydrocryptopine (A) (2 grams) in warm benzene reacts readily with methyl sulphate (2 c.c.) with considerable rise of temperature, and, if a crystal of the methosulphate is introduced and the whole allowed to remain in the ice-chest, a hard crust of nodules separates. If a crystal is not available, the methosulphate generally separates as a syrup, which, however, after washing with ether and stirring with ether, rapidly crystallises. For analysis, the substance was recrystallised from water, in which it is readily soluble; it separates in groups of short, prismatic needles:

0·1177 gave 0·2460 CO_2 and 0·0646 H_2O. C=57·1; H=6·1.

$C_{21}H_{23}O_4N,Me_2SO_4$ requires C=57·6; H=6·1 per cent.

ψ-Anhydrodihydrocryptopine (A) *methosulphate* melts at 175—180° with some effervescence, but without darkening; the solution of a trace in acetic acid gives with sulphuric acid a deep burnt sienna coloration, becoming intense permanganate on the addition of a drop of dilute nitric acid. It is readily soluble in hot methyl alcohol, and when boiled with methyl-alcoholic potassium hydroxide, the solution becomes deep violet, especially where it comes in contact with the air; the colour then changes to bluish-violet, then to sage-green; the addition of hydrochloric acid destroys the green colour and yields a clear, burnt sienna solution.

The *Methiodide*, $C_{21}H_{23}O_4N,MeI$.—The addition of hot dilute potassium iodide to the hot dilute solution of the methosulphate results in a clear solution, from which the methiodide immediately begins to separate in well-developed, six-sided prisms with bevelled edges:

0·1172 gave 0·2315 CO_2 and 0·0602 H_2O. C=53·9; H=5·7.

$C_{21}H_{23}O_4N,MeI$ requires C=53·3; H=5·3 per cent.

ψ-Anhydrodihydrocryptopine methiodide is sparingly soluble in boiling methyl alcohol, and separates in long, prismatic needles radiating from a centre. It melts at 197—200°, with vigorous effervescence to a yellow froth.

Oxidation of ψ-Anhydrodihydrocryptopine (A).—When this base (2 grams) was treated in acetone solution with powdered permanganate (2·5 grams), it was noticed that oxidation was slow, and, on working up the product, about half the substance was

recovered unchanged. The aqueous extract from the manganese precipitate yielded, on concentrating and acidifying, a small quantity of a highly coloured acid resembling amorphous phosphorus, and this did not appear to contain any 5:6-methylene-dioxy-*o*-toluic acid (compare p. 728).

$$\psi\text{-}Cryptopidene, \qquad \overset{\overset{\displaystyle ...}{CH:C-}}{\underset{CHMe}{\bigvee}} Me .$$
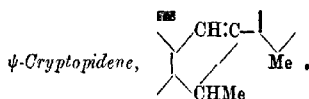
This characteristic substance is produced directly from ψ-anhydro-dihydrocryptopine (A) methosulphate by reduction with sodium amalgam in faintly alkaline solution. The methosulphate (8 grams), dissolved in hot water (200 c.c.), was poured on crushed sodium amalgam (150 grams of 3 per cent.) in a flat basin, when, on heating on the steam-bath, there was an immediate odour of dimethylamine, and a crystalline scum began to rise to the surface. After about half an hour, there was no further separation; the whole was therefore filtered, and the colourless, crystalline residue washed and recrystallised from methyl alcohol. The yield appeared to be almost that theoretically possible:

0·1121 gave 0·3052 CO_2 and 0·0628 H_2O. $C=74·2$; $H=6·2$.

$C_{20}H_{20}O_4$ requires $C=74·1$; $H=6·2$ per cent.

ψ-*Cryptopidene* melts at 142—144°, and cannot be identical with *iso*-ψ-cryptopidene (m. p. 152°, p. 776), since the mixture of the two substances melts at about 130—132° with previous softening. It is sparingly soluble in cold methyl alcohol, but dissolves more readily on boiling, and separates in groups of nearly colourless, glistening needles. It dissolves readily in boiling alcohol, benzene, acetone, or acetic acid, but is sparingly soluble in ether or light petroleum. It crystallises well from light petroleum in six-sided plates, and from acetone or dilute acetic acid in needles. The solution of a trace in acetic acid gives, with sulphuric acid, a burnt sienna coloration which, on the addition of a drop of dilute nitric acid, becomes deep brown. Concentrated nitric acid dissolves the substance to a deep brown solution, which gradually fades. A crystal of the substance dissolved in acetic acid gives, with manganese dioxide and dilute sulphuric acid, an intense brown solution.

ψ-Cryptopidene does not appear to be reduced when its solution in boiling alcohol is treated with sodium (compare p. 745).

Oxidation of ψ-Cryptopidene.—In this experiment, the substance (3·5 grams), dissolved in acetone (200 c.c.), was oxidised by the gradual addition of finely powdered permanganate (5 grams) at

the ordinary temperature. The product was filtered, and the manganese precipitate, after thoroughly washing with acetone, extracted with boiling water. The brown, alkaline extract was nearly neutralised, boiled with animal charcoal, concentrated, and acidified, when an acid (0·5 gram) separated which crystallised from acetic acid in needles, melted at 214—216°, and was recognised as 5 : 6-methylenedioxy-o-toluic acid (916). The acetone extract from the oxidation yielded, on evaporation, a syrupy mass (2·9 grams), which, when rubbed with methyl alcohol, immediately crystallised. After filtering and leaving in contact with porous porcelain, the yellow mass was once crystallised from methyl alcohol, when it separated in pale yellow needles melting at about 128°. On careful fractional crystallisation from methyl alcohol, three distinct kinds of crystals were observed; these were mechanically separated, and each kind was recrystallised. The three constituents were found to be (i) unchanged ψ-cryptopidene melting at 140—142°; *dioxy-ψ-cryptopidene*, $C_{20}H_{18}O_6$, melting at 138—140° and crystallising in light, woolly balls; *trioxy-ψ-cryptopidene*, $C_{20}H_{18}O_7$, melting at 165° and crystallising in hard, single, sulphur-yellow prismatic needles.

The analysis of *dioxy-ψ-cryptopidene* yielded the following results :

0·1071 gave 0·2640 CO_2 and 0·0481 H_2O. C=67·2; H=5·2.

$C_{20}H_{18}O_6$ requires C = 67·8; H = 5·1 per cent.

The solution of a trace of this substance in acetic acid gives with sulphuric acid an intense brown coloration, becoming purplish-brown and then cherry-red on the addition of a drop of dilute nitric acid. It reacts readily when its solution in methyl alcohol is boiled with excess of semicarbazide hydrochloride and sodium acetate, and a crystalline precipitate of the *semicarbazone* separates which is very sparingly soluble in methyl alcohol.

Found: N = 11·3.

$C_{21}H_{21}O_6N_3$ requires N = 10·2 per cent.

The behaviour of dioxy-ψ-cryptopidene towards alkalis resembles that of benzoin or benzil. Methyl-alcoholic potassium hydroxide does not immediately colour the substance, but gradually a reddish-brown develops, and, on warming, this becomes intense reddish-brown, then pink, and then gradually fades.

The product, diluted with water, yields a pale brown solution, and hydrochloric acid precipitates an amorphous acid which, on warming, becomes crystalline.

Trioxy-ψ-cryptopidene (m. p. 165°) yielded the following analytical results:

0.1070 gave 0.2539 CO_2 and 0.0478 H_2O. $C=64.7$; $H=5.0$.

$C_{20}H_{18}O_7$ requires $C=64.9$; $H=4.9$ per cent.

The acetic acid solution of a trace of this substance is coloured yellowish-brown by sulphuric acid, and the addition of a drop of dilute nitric acid changes this first to port-wine colour and then to intense burnt sienna. It also reacts very readily when its solution in boiling methyl alcohol is mixed with excess of a saturated aqueous solution of semicarbazide hydrochloride and sodium acetate, and a voluminous, rather gelatinous precipitates separates which appears to be the *disemicarbazone* mixed probably with some of the mono-derivative.

Found: $N = 15.7$.

$C_{21}H_{21}O_7N_3$ requires $N = 9.8$; $C_{22}H_{24}O_7N_6$ requires $N = 17.3$ per cent.

Trioxy-ψ-cryptopidene, like the corresponding dioxy-derivative (see above), exhibits the benzil reaction in a striking manner. The powdered substance is rapidly coloured brown when mixed with methyl-alcoholic potassium hydroxide, and dissolves to an intense reddish-brown solution, which becomes pink in contact with air, and then soon fades, but not completely. The solution of the product in water is pale salmon, and yields a brick-red, crystalline precipitate on the addition of dilute hydrochloric acid.

Constitutional formulæ which appear to be in harmony with the properties of dioxy- and trioxy-ψ-cryptopidene are suggested on p. 729.

Section IV (b).   *The Reduction of ψ-Cryptopine Chloride in Acid Solution: Formation of Dihydroanhydro-ψ-cryptopine* (I) *and* iso-ψ-Cryptopidene (II),
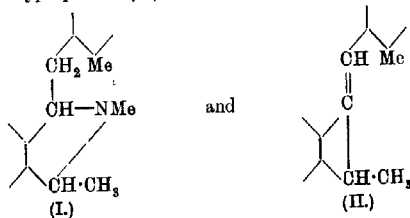
In studying this curious reduction, ψ-cryptopine chloride (5 grams), dissolved in water (80 c.c.) and concentrated hydrochloric acid (15 c.c.), was treated at the boiling témperature, in an enamelled iron basin, with sodium amalgam (200 grams of 4 per cent.), which was added all at once. The whole was well

stirred during the reduction, and care was taken, by frequently adding small quantities of hydrochloric acid, that the liquid was always strongly acid. During the process, a white, crystalline, insoluble substance (iso-ψ-cryptopidene) separated in quantity equal to about 8 per cent. of the ψ-cryptopine chloride employed; this was collected, and its examination is described on p. 776.

The acid filtrate from this neutral substance was mixed with excess of ammonia, when a caseous precipitate separated which, on shaking, became chalky, and this was collected, washed, and drained on porous porcelain. The nearly colourless mass was dissolved in methyl alcohol and poured into a large volume of ether, when a flocculent precipitate of unchanged ψ-cryptopine chloride separated, which was collected and well washed with ether. The pale brown ethereal filtrate was washed with water until free from methyl alcohol, dried over potassium carbonate, and concentrated to a small bulk, but nothing separated after remaining in the ice-chest for a week. When the ether was evaporated, a syrup remained which, over phosphoric oxide in a vacuum desiccator, became a friable mass like colophony, and consisted of almost pure dihydroanhydro-ψ-cryptopine:

0·1265 gave 0·3271 CO_2 and 0·0806 H_2O. C=70·5; H=7·0.

$C_{21}H_{25}O_4N$ requires C=71·0; H=7·0 per cent.

All attempts to obtain this base in a crystalline condition were unsuccessful, and it is fortunate that it yields a characteristic picrate which separates as a deep ochreous, amorphous precipitate when picric acid is added to the aqueous solution of the hydrochloride. This double salt melts under boiling water, and is sparingly soluble in boiling methyl alcohol, from which it separates in deep orange leaflets. After drying in the steam-oven, the substance becomes yellow at 110°, shrinks at 180°, and melts at about 195—197° to a reddish-brown syrup:

0·1021 gave 8·7 c.c. N_2 at 13° and 755 mm. N=10·0.

$C_{21}H_{25}O_4N,C_6H_3O_7N_3$ requires N=9·6 per cent.

This picrate was decomposed by ammonia, the base extracted with ether, the ethereal solution washed, dried over potassium carbonate, evaporated, and the syrup left over phosphoric oxide in a vacuum desiccator until it became a friable resin and the weight was constant. The analysis then yielded C=70·9; H=7·0, agreeing well with the formula $C_{21}H_{25}O_4N$, which requires C=71·0; H=7·0 per cent.

Oxidation of Dihydroanhydro-ψ-cryptopine.—When the solution of the base (1 gram) in acetone is treated with finely divided permanganate (1·2 grams), oxidation takes place moderately readily at 15°.

The manganese precipitate, after thoroughly washing with acetone, yielded on extraction with hot water a deep brown solution, from which hydrochloric acid precipitated a dark, resinous acid. This was collected, boiled with much water, the extract decolorised with animal charcoal, neutralised with sodium carbonate, and evaporated to a small bulk.

On acidifying the nearly colourless solution, a chalky acid separated, which crystallised from acetic acid as a colourless, satiny mass, melted at 214—216°, and was recognised as 5 : 6-methylene-dioxy-*o*-toluic acid, $CH_2:O_2:C_6H_2Me\cdot CO_2H$ (916). The acetone solution from the oxidation deposited a syrup on evaporation which was only partly soluble in warm dilute hydrochloric acid, but the amount was too small for further investigation.

iso-ψ-Cryptopidene, $C_{20}H_{20}O_4$.—The neutral substance formed during the reduction of ψ-cryptopine chloride (see above) was well washed, dried on porous porcelain, and twice recrystallised from methyl alcohol :

0·1047 gave 0·2838 CO_2 and 0·0598 H_2O. C = 73·9 ; H = 6·3.
0·1023   „   0·2768 CO_2 „ 0·0553 H_2O. C = 73·8 ; H = 6·0.
$C_{20}H_{20}O_4$ requires C = 74·1 ; H = 6·0 per cent.

iso-ψ-Cryptopidene melts at 150—152°, and is moderately soluble in boiling methyl alcohol, from which it crystallises in glistening plates resembling benzoic acid. It dissolves readily in benzene, but is almost insoluble in light petroleum, and separates, when the hot solution in benzene is mixed with light petroleum, in thin, rhombic plates.

It also crystallises well from acetone in almost square plates with bevelled edges. It is readily soluble in boiling glacial acetic acid, much less so in the cold, and separates splendidly as a satiny mass of thin, rectangular plates. The solution of a crystal in a drop of acetic acid gives, on the addition of sulphuric acid, a deep brown coloration, which becomes much more intense on adding a drop of dilute nitric acid.

A trace of the substance rubbed on a watch-glass dissolves in concentrated nitric acid, and the intense indigo-blue coloration produced soon changes to brown. The most characteristic reaction of the substance is the intense pink colour, changing to brown, which develops when finely powdered manganese dioxide and a little dilute sulphuric acid is added to the solution in dilute acetic acid. *iso-ψ*-Cryptopidene does not appear to be readily reduced when its solution in boiling alcohol is treated with sodium.

Oxidation of iso-ψ-Cryptopidene to Ketodihydroiso-ψ-crypto-pidene.—*iso-ψ*-Cryptopidene is scarcely attacked when its solution in acetone is mixed with permanganate at −10°, and action is

very slow even at the ordinary temperature. In order to study this oxidation, the substance (1·4 grams), dissolved in acetone (50 c.c.), was, during two days, gradually mixed with very finely powdered and sieved permanganate (2 grams).

The product was filtered, the manganese precipitate thoroughly washed with acetone (*B*), and extracted with boiling water. The brown, aqueous solution was decolorised with animal charcoal, concentrated, and acidified, when a small quantity of a solid acid separated which crystallised from acetic acid in satiny plates, melted at 215—217°, and consisted of 5 : 6-methylenedioxy-*o*-toluic acid (916).

The acetone solution (*B*) deposited, on evaporation, a yellow syrup, and this yielded, when distilled in a current of steam, a small quantity of 5 : 6-methylenedioxy-*o*-tolualdehyde (907), which separated from the distillate in needles and melted at 72—74°. The residue in the steam distillation flask was extracted with ether, the ethereal solution thoroughly dried over potassium carbonate, and evaporated, when a syrup remained, which soon crystallised. After remaining in contact with porous porcelain until oily impurity had been removed, the almost colourless residue was fractionally crystallised from methyl alcohol, and thus separated into unchanged *iso-ψ*-cryptopidene and a new substance, which crystallised in glistening plates, melted at about 135°, and consisted of *ketodihydro*iso-*ψ*-*cryptopidene*. Unfortunately, the small amount of material available did not allow of the removal of the last traces of *iso-ψ*-cryptopidene, so that the melting point must be taken as approximate only :

0·1102 gave 0·2861 CO_2 and 0·0589 H_2O. C = 70·8 ; H = 5·9.

$C_{20}H_{20}O_5$ requires C = 70·6 ; H = 5·9 per cent.

The small remainder of the substance was dissolved in boiling methyl alcohol, digested with excess of semicarbazide hydrochloride and sodium acetate for two hours, and evaporated to dryness. The nearly white residue was washed with water and crystallised from alcohol, from which it separated in needles :

0·1001 gave 0·2348 CO_2 and 0·0522 H_2O. C = 64·0 ; H = 5·9.

$C_{21}H_{23}O_5N_3$ requires C = 63·5 ; H = 5·8 per cent.

Attempts to hydrolyse this *semicarbazone* with a view to obtaining the pure keto-derivative were unsuccessful, since boiling with concentrated hydrochloric acid converts it into a substance which crystallises from methyl alcohol in needles, melts at about 225°, and is possibly an indole derivative. A constitutional formula for ketodihydro*iso*-*ψ*-cryptopidene is suggested on p. 730.

Section IV (c). *The Reduction of ψ-Methylberberinium Chloride: Formation of* iso-ψ-*Berberidene and Dihydroanhydro-ψ-methyl-berberine.*

This reduction was carried out essentially under the conditions described in detail in the case of the acid reduction of ψ-cryptopine chloride (p. 774), 300 grams of 4 per cent. amalgam being employed for the reduction of 8 grams of the chloride. During the process, a scum separated, which at first was crystalline, but later melted to a brown syrup, and, after the product had cooled, this was extracted with ether (*A*), the ethereal solution well washed, dried over potassium carbonate, and evaporated, when a syrup remained which showed no signs of crystallising. However, on rubbing with methyl alcohol, crystallisation soon commenced, and, after collecting and washing with methyl alcohol, the pale salmon mass was twice recrystallised from this solvent:

$0 \cdot 1187$ gave $0 \cdot 3207$ CO_2 and $0 \cdot 0677$ H_2O. $C = 73 \cdot 7$; $H = 6 \cdot 3$.
$0 \cdot 1195$,, $0 \cdot 3245$ CO_2 ,, $0 \cdot 0687$ H_2O. $C = 74 \cdot 1$; $H = 6 \cdot 4$.
$C_{20}H_{20}O_4$ requires $C = 74 \cdot 1$; $H = 6 \cdot 2$ per cent.

iso-ψ-*Berberidene* melts at 117° and is sparingly soluble in methyl alcohol, yielding a lilac, fluorescent solution, from which it separates in well-developed prismatic needles. It is very readily soluble in benzene, but less so in light petroleum, and separates from the mixture of these solvents particularly well in brilliant, elongated prisms. It also crystallises well from light petroleum alone or from ether, in which it is readily soluble, or from acetic acid, in glistening prisms.

A trace of the substance rubbed on the side of a test-tube is coloured deep violet, changing to brown by concentrated nitric acid.

The solution in acetic acid is coloured yellowish-brown on the addition of sulphuric acid, and a drop of dilute nitric acid changes the colour to an intense reddish-brown. When manganese dioxide and a little dilute sulphuric acid are added to the solution in acetic acid in the cold, a pink colour gradually develops, and, on warming, this changes to brown and then to yellow. The relationship of iso-ψ-berberidene and *iso*-ψ-cryptopidene is discussed on p. 731, and it may be pointed out that the striking similarity in their properties is doubtless due to their both containing the characteristic grouping

$$\underset{\text{CH·CH}_3}{\overset{\text{CH}\quad\text{Me}}{\overset{\|}{\underset{\text{C}}{}}}}$$

$$Dihydroanhydro\text{-}\psi\text{-}methylberberine,\qquad \underset{\text{CH·CH}_2}{\overset{\text{CH}_2\text{Me}}{\underset{\text{CH—NMe.}}{}}}$$
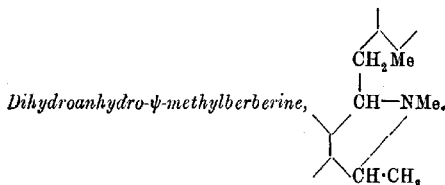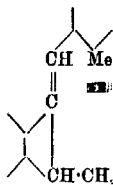
The acid liquors (*A*) from the reduction of ψ-methylberberinium chloride, which had been extracted with ether, as already described, were made strongly alkaline with ammonia, and the turbid liquid thoroughly extracted with ether. On evaporation, the ethereal solution deposited a syrup, which was only partly soluble in dilute hydrochloric acid.

The whole was warmed with very dilute hydrochloric acid, filtered, and the filtrate precipitated with excess of picric acid, when a voluminous, viscid mass separated, which soon hardened. This was collected, left on porous porcelain until dry, and recrystallised from methyl alcohol, from which it separated in orange-red balls, and melted at 115—120° to an orange-red syrup:

0·1108 gave 0·2286 CO_2 and 0·0469 H_2O. C=56·1; H=4·7.

0·1027 ,, 8·6 c.c. N_2 at 14° and 756 mm. N=9·8.

$C_{21}H_{25}O_4N, C_6H_3O_7N_3$ requires C=55·5; H=4·7; N=9·6 per cent.

This *picrate* was decomposed by warming with dilute ammonia, the base extracted with ether, the ethereal solution thoroughly washed, dried over potassium carbonate, and evaporated, when a syrup remained which, over phosphoric oxide in a vacuum desiccator, dried to a friable resin:

0·1271 gave 0·3292 CO_2 and 0·0817 H_2O. C=70·6; H=7·1.

$C_{21}H_{25}O_4N$ requires C=71·0; H=7·0 per cent.

Dihydroanhydro-ψ-methylberberine exhibits little tendency to crystallise, but it seems to become crystalline when left in a closed tube in contact with a little methyl alcohol. The hydrochloride is very readily soluble and gives, on the addition of platinic chloride, an ochreous, caseous precipitate of the *platinichloride* which, on warming, becomes chalky:

0·1217 gave 0·2040 CO_2 and 0·0521 H_2O.   C=45·7; H=4·7.
0·2054   „   0·0351 Pt.   Pt=17·1.
$(C_{21}H_{25}O_4N)_2,H_2PtCl_6$ requires C=45·1; H=4·7; Pt=17·3 per cent.
  The addition of boiling dilute aqueous potassium iodide to the boiling dilute solution of the hydrochloride gave a milky liquid, from which a yellow syrup separated. This dissolved readily in methyl alcohol, and the solution, on spontaneous evaporation, deposited a crystalline mass of the *hydriodide*, which was drained on porous porcelain, dried in the steam-oven, and analysed:

0·1117 gave 0·2141 CO_2 and 0·0539 H_2O.   C=52·2; H=5·3.
$C_{21}H_{25}O_4N,HI$ requires C=52·2; H=5·4 per cent.

Section V.

Derivatives of iso*Anhydrocryptopine*,
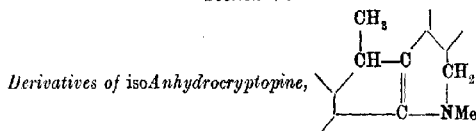
  The *iso*anhydrocryptopine required for these experiments was prepared by the method already given (1002), and certain direct derivatives of this substance, not previously described, were obtained during the course of the investigation.
  iso*Anhydrocryptopine   Methochloride*, $C_{21}H_{21}O_4N,MeCl$.—This characteristic derivative is readily obtained when *iso*anhydro-cryptopine methiodide (1005), ground to a paste with much water, is digested on the steam-bath with excess of silver chloride for an hour. The filtrate, on concentration, deposits the methochloride as a hard crust of pale lemon-yellow prisms; after remaining exposed to the air until the weight was constant, this quaternary salt contained two molecules of water, and became opaque on drying at 100°:
  1·7754 lost 0·1493 at 100°. H_2O=8·4.
    $C_{21}H_{21}O_4N,MeCl,2H_2O$ contains H_2O=8·2 per cent.
  0·1075 (dried at 100°) gave 0·2577 CO_2 and 0·0575 H_2O.
    C=65·4; H=5·9.
    $C_{21}H_{21}O_4N,MeCl$ requires C=65·7; H=6·0 per cent.
  iso*Anhydrocryptopine methochloride* melts at about 233° with vigorous decomposition to a black froth. It is very readily soluble in hot, but much less so in cold, water, and the addition of hydrochloric acid does not appear greatly to reduce the solubility. The aqueous solution gives no precipitate with ammonia or dilute sodium hydroxide.

The anhydrous salt dissolves readily in boiling methyl alcohol and separates, on cooling, in long, flat prisms which are quite colourless.

When the cold aqueous solution is mixed with dilute sulphuric acid and then a little manganese dioxide dusted in, a pale blue coloration gradually develops, which deepens on warming. The addition of dilute permanganate at 0° to the aqueous solution produces at first a purple precipitate of the permanganate, and then oxidation rapidly takes place.

*Dihydro*isoanhydrocryptopine,

$$
\begin{array}{c}
\text{CH}_3 \\
| \\
-\text{CH}\!-\!\text{CH} \quad \text{CH}_2 \\
| \\
-\text{CH}\!-\!\text{NMe}
\end{array}
$$
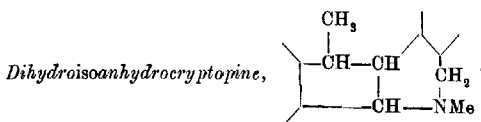
This base was obtained by the reduction of *iso*anhydrocryptopine under the following conditions. The hydrochloride of *iso*anhydrocryptopine* (1004) (3 grams), dissolved in dilute acetic acid and sodium acetate, was gradually treated with crushed sodium amalgam (200 grams of 3 per cent.) at about 80°. When the amalgam was exhausted, the filtered solution was mixed with ammonia, the chalky precipitate collected, and dissolved in hot dilute hydrochloric acid. On long keeping in the ice-chest, the very sparingly soluble *hydrochloride* of *dihydro*isoanhydrocryptopine separated, and was collected and recrystallised from dilute hydrochloric acid,† from which it separates in groups of colourless prisms; it darkens at 210° and decomposes at about 215—218° with vigorous effervescence to an orange-red froth:

0·1101 gave 0·2619 CO_2 and 0·0625 H_2O. C = 64·5; H = 6·3.

$C_{21}H_{23}O_4N$,HCl requires C = 64·7; H = 6·2 per cent.

This hydrochloride is comparatively readily soluble in hot water, but very sparingly so in dilute hydrochloric acid. The base, obtained by adding ammonia to the dilute aqueous solution of the hydrochloride, is a gelatinous precipitate becoming granular on warming, but all attempts to recrystallise the substance were unsuccessful. The precipitate, thoroughly washed, was dried over phosphoric oxide in a vacuum desiccator:

* This hydrochloride, like that of anhydrocryptopine (977), is dissociated when sodium acetate is added to its aqueous solution.

† The mother liquors of this hydrochloride contain the hydrochloride of a second base which also has the composition $C_{21}H_{23}O_4N$, and it is probable that the two bases represent stereoisomeric modifications of the same substance.

0·1070 gave 0·2801 CO_2 and 0·0621 H_2O. $C=71·2$; $H=6·4$
$C_{21}H_{23}O_4N$ requires $C=71·4$; $H=6·5$ per cent.

Section V (a). *The Reduction of* iso*Anhydrocryptopine Metho-
sulphate in Alkaline Solution* (p. 732): *Formation of Dihydro-
methyl*iso*anhydrocryptopine,* (*A*) *and* (*B*),
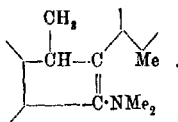
The isoanhydrocryptopine methosulphate used in these experi-
ments was prepared by adding methyl sulphate to the benzene
solution of isoanhydrocryptopine in the manner already described
(1005). The carefully purified substance (5 grams), dissolved in
boiling water (300 c.c.), was vigorously stirred with crushed sodium
amalgam (150 grams of 3 per cent.), when a base separated, some
times in crystalline form, but more frequently as a gum, which
ultimately crystallised. The whole was heated on the steam-bath
until no further separation could be observed; the base was then
collected, washed well, dried on porous porcelain, and dissolved in
boiling methyl alcohol. When this solution is allowed to remain
without agitation, the modification (*A*) of *dihydromethyl*iso-
anhydrocryptopine separates as a bulky mass of soft needles, but
gradually pale yellow prisms of the modification (*B*) make their
appearance, and, if the hot solution is stirred during crystallisa-
tion, the separation consists entirely of this modification. The
prisms (*B*) melt sharply at 121—122°, but, when the needles (*A*)
are slowly heated in a capillary tube, it is noticed that they sinter
at about 105°, clearly owing to transition into the prismatic modifi-
cation, and the melting point is again 121—122°. Both modifica-
tions were analysed:

(*A*) 0·1098 gave 0·2908 CO_2 and 0·0687 H_2O. $C=72·2$;
     $H=7·0$.
(*B*) 0·1101 gave 0·2906 CO_2 and 0·0685 H_2O. $C=72·0$;
     $H=6·9$.
     $C_{22}H_{25}O_4N$ requires $C=71·0$; $H=6·8$ per cent.

Crystals of this substance were kindly examined by Miss M. W.
Porter, who reports that the system is anorthic, with $a:b:c=$
$0·728:1:0·766$, $a=100°15'$, $\beta=104°23'$, $\gamma=95°2'$. The following
forms were observed: $b(010)$, $a(100)$, $c(001)$, $q(0\bar{1}1)$, $r(\bar{1}01)$, and
$p(\bar{1}11)$. The habit, as is shown in Fig. 4, is prismatic, and the

vertical faces are generally curved.   Following are the mean
measurements derived from three crystals:

	Azimuth.	Polar distance.
b (010)	0° 0′	90° 0′
a (100)	*82 2	90 0
c (001)	*49 33	*18 37
q (0$\bar{1}$1)	155 8	32 25
r ($\bar{1}$01)	275 24	39 25
q ($\bar{1}\bar{1}$1)	*229 4	*47 42

FIG. 4.
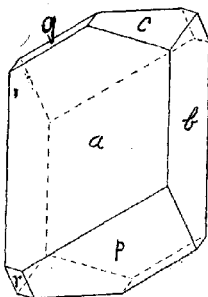
*Dihydromethyl*isoanhydrocryptopine (B). m. p. 122°.

The solution of a trace of either modification in a drop of acetic
acid gives with sulphuric acid a deep orange-red coloration, which
becomes intense port wine and then brown on the addition of
dilute nitric acid.   *Dihydromethyl*isoanhydrocryptopine is very
readily soluble in cold dilute hydrochloric acid, but, on rubbing,
the sparingly soluble crystalline hydrochloride immediately
separates.   This fine salt is readily soluble in hot water, and crystal-
lises in short, six-sided prisms with obliquely cut-off ends.   The
sulphate does not crystallise under these conditions, but the addi-
tion of dilute nitric acid to the solution of the sulphate causes the
nitrate to separate as a syrup, which crystallises on rubbing.

The Methosulphate.—This characteristic derivative is readily
prepared by adding methyl sulphate (3 c.c.) to the solution of the
base (2·5 grams) in a little warm benzene, when combination takes
place immediately with the evolution of much heat.   The liquid
soon becomes a pasty mass of crystals, and these are collected,
washed with benzene, and recrystallised from water or methyl
alcohol:

0·1094 gave 0·2334 CO_2 and 0·0623 H_2O.   C=58·2; H=6·3.

$C_{22}H_{25}O_4N,Me_2SO_4$ requires C=58·4; H=6·3 per cent.

*Dihydromethyl*iso*anhydrocryptopine   methosulphate* melts at about 202°, without effervescence, to a colourless syrup, and is readily soluble in hot water, from which it separates in groups of flat needles; the aqueous solution gives no precipitate on the addition of ammonia. It dissolves very readily in boiling methyl alcohol, but is much less soluble in the cold and separates in thin plates with obliquely cut-off ends. When warmed with methyl-alcoholic potassium hydroxide (15 per cent.), it dissolves, and, on boiling, decomposition slowly sets in with the elimination of trimethylamine; the liquid becomes brown, then deep purple, and finally nearly black, and the addition of water then precipitates a black substance (compare 985).

The Methiodide.—The addition of hot dilute potassium iodide to the hot dilute solution of the methosulphate produces no immediate precipitate, but the liquid soon clouds, and a gum separates which, on rubbing, readily crystallises. If this gum is dissolved in boiling alcohol and the solution stirred, the methiodide separates as a sandy precipitate consisting of curious, circular warts:

0·1121 gave 0·2215 CO_2 and 0·0563 H_2O.   C = 53·9; H = 5·6.

$C_{32}H_{25}O_4N,MeI$ requires C = 54·2 ; H = 5·5 per cent.

This *methiodide* melts at about 215—217° to a yellow syrup.

*ψ-Dihydromethyl*iso*anhydrocryptopine* (p. 732),
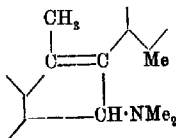
This substance is obtained (*a*) from *iso*anhydrocryptopine methochloride (p. 780) by reduction in hydrochloric acid solution with sodium amalgam, or (*b*) from dihydromethyl*iso*anhydrocryptopine by boiling with dilute hydrochloric acid.   (*a*) *iso*Anhydrocryptopine methochloride (3 grams), dissolved in hot water (200 c.c.) and hydrochloric acid (30 c.c.), is treated with sodium amalgam (120 grams of 4 per cent.) on the steam-bath.   When reduction is complete, the liquid is filtered from a trace of a chalky, neutral substance, the filtrate mixed with ammonia, the rather gelatinous precipitate collected, washed, dried on porous porcelain, and dissolved in a little boiling methyl alcohol, in which it is very readily soluble. If the solution is cooled in ice and salt and rubbed, crystallisation gradually sets in, and, on recrystallisation, pure *ψ-dihydromethyl*-iso*anhydrocryptopine* is obtained in colourless needles melting at

140—141°. (*b*) Dihydromethyl*iso*anhydrocryptopine (1 gram), dissolved in concentrated hydrochloric acid (2 c.c.) and water (10 c.c.), is boiled for ten minutes in an open test-tube by means of a sulphuric-acid bath in such a way that concentration to about half the volume takes place. At first there is no visible change, but towards the end of the operation a pale green develops. The cold product yields a caseous precipitate on the addition of ammonia, which soon becomes hard, and the substance separates from methyl alcohol in microscopic groups of needles melting at 140—141°. Analyses were made with substances prepared by methods (*a*) and (*b*):

(*a*) 0·1238 gave 0·3271 CO_2 and 0·0776 H_2O. C=72·0; H=6·9.
(*b*) 0·1250 „ 0·3298 CO_2 „ 0·0783 H_2O. C=71·9; H=6·9.

$C_{22}H_{25}O_4N$ requires C=71·9; H=6·8 per cent.

ψ-*Dihydromethyliso*anhydrocryptopine is sparingly soluble in cold methyl alcohol and not very readily so on boiling; it is also rather sparingly soluble in cold acetone, but dissolves on boiling and separates in groups of glistening needles; it is easily soluble in benzene, even in the cold. The solution of a crystal in a drop of acetic acid gives, with sulphuric acid, a deep orange coloration, which becomes intense port wine on the addition of a drop of dilute nitric acid. A characteristic of the base is its remarkable resistance to reduction, since experiment showed that much remains unchanged after its solution in dilute hydrochloric acid has been boiled with a large excess of sodium amalgam (compare p. 733).

It is also oxidised with unusual difficulty when permanganate is added to its solution in acetone.

The Methosulphate.—A considerable rise of temperature takes place when methyl sulphate is added to the solution of the base in warm benzene, and the methosulphate begins to separate immediately as a chalky mass. This was collected, washed with benzene, and analysed :

0·1092 gave 0·2332 CO_2 and 0·0626 H_2O. C=58·1; H=6·4.

$C_{22}H_{25}O_4N,Me_2SO_4$ requires C=58·4; H=6·3 per cent.

ψ-*Dihydromethyliso*anhydrocryptopine methosulphate melts at about 188—190°, and is sparingly soluble in water or methyl alcohol in the cold, but dissolves readily on warming and separates in colourless groups of needles. It is decomposed with some difficulty by boiling methyl-alcoholic potassium hydroxide (15 per cent.), trimethylamine is eliminated, and, on the addition of water, a chalky substance separates, which was not further examined.

Reduction of the Methosulphate.—When crushed sodium amalgam was added to the cold aqueous solution of the metho-

sulphate at about 50°, the odour of trimethylamine became at once apparent, and a chalky substance separated. After keeping at 50° for some hours, with constant stirring, the precipitate was collected, and found to melt at 160—163°. It was recrystallised from methyl alcohol, in which it was remarkably sparingly soluble, and then melted at 166—167°. That this substance is iso*cryptopidene* (*A*),

$$\begin{array}{c} \text{CH}_3 \\ \mid \\ \text{C}\!=\!\!\!=\!\text{C} \quad \text{Me} \\ \\ \text{CH}_2 \end{array}$$
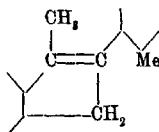
that is to say, is identical with the substance which results from the cold reduction of dihydromethyl*iso*anhydrocryptopine methosulphate (see below), was proved by a comparison of properties, and particularly by the fact that the mixture of the two substances melted at 166—167°.

The iso*Cryptopidenes*, (*A*) *and* (*B*),

$$\begin{array}{ccc} \text{CH}_3 & & \text{CH}_3 \\ \mid & & \mid \\ \text{C}\!=\!\!\!=\!\text{C} \quad \text{Me} & \text{and} & \text{CH}\!-\!\text{C} \quad \text{Me} \\ & & \\ \text{CH}_2 & & \text{CH} \end{array}$$

(*A*.) M. p. 167°.   (*B*.) M. p. 108°.
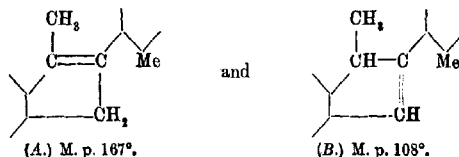
The difficulty of completely understanding the mechanism of the formation of these curious and interesting substances is referred to in the introduction to this paper (p. 733), and reasons are there given for assigning the above formulæ to the two isomerides.

iso*Cryptopidene* (*A*) (m. p. 167°) is produced by the reduction (i) of the methosulphate of dihydromethyl*iso*anhydrocryptopine, or (ii) of the methosulphate of ψ-dihydromethyl*iso*anhydrocryptopine in alkaline solution and also by the reduction of ψ-dihydromethyl*iso*-anhydrocryptopine in acid solution. The method of formation (ii) has just been described, but the method of preparation which is probably most convenient is that stated under (i). In this reduction, dihydromethyl*iso*anhydrocryptopine methosulphate (2 grams, p. 783), dissolved in water (150 c.c.), is poured on freshly prepared crushed sodium amalgam (100 grams of 3 per cent.) in a porcelain beaker fitted with a mechanical stirrer, and the reduction carried out at a temperature not exceeding 30°. The odour of trimethylamine becomes immediately apparent, and a chalky precipitate of *iso-*

cryptopidene (A) gradually forms, but the separation is not complete until the stirring has been continued for two days. The precipitate is then collected, washed with water, and dried in the steam-bath, when it melts at 163—165°, and is almost pure *iso*cryptopidene (A), the yield being very good. For analysis, the substance was recrystallised from much methyl alcohol, and considerable difficulty was experienced in obtaining accurate results:

0·1195 gave 0·3231 CO_2 and 0·0654 H_2O.   C = 73·7; H = 6·1.

0·1075 „ 0·2901 CO_2 „ 0·0584 H_2O.   C = 73·6; H = 6·0.

$C_{20}H_{20}O_4$ requires C = 74·1; H = 6·2 per cent.

iso*Cryptopidene* (A) melts at 166—167°, and is remarkably sparingly soluble in boiling methyl alcohol, from which it separates as a sandy powder consisting of well-developed, glistening prisms; it is also very sparingly soluble in boiling alcohol or acetone, and separates from the latter in striated prisms. The solution of a crystal in a few drops of glacial acetic acid gives with sulphuric acid a deep orange coloration, which changes to red on the addition of a drop of nitric acid.

(iii) *The Reduction of ψ-Dihydromethyl*iso*anhydrocryptopine* (p. 784) *in Acid Solution.*—In carrying out this experiment dihydromethyl*iso*anhydrocryptopine (5 grams) (m. p. 122°, p. 782) was dissolved in a large excess of boiling dilute hydrochloric acid, and thus converted into the ψ-isomeride (p. 785). Freshly prepared sodium amalgam (250 grams of 4 per cent.) was then added to the boiling solution, when a small amount of a chalky precipitate separated, which was collected, washed well, and dried in the steam-oven. In this condition, it melted at 162—165°, and, after recrystallisation from methyl alcohol, in which it was very sparingly soluble, at 166—167°. The careful comparison of the properties of this substance with those of the specimen of *iso*cryptopidene (A) obtained from the alkaline reduction of dihydromethyl*iso*anhydrocryptopine methosulphate (see above) clearly indicated identity, and this was confirmed by the observation that the mixture of the two preparations melted at 166—167°.

The yield of *iso*cryptopidene (A) obtained by reducing ψ-dihydromethyl*iso*anhydrocryptopine in acid solution is only about 8 per cent. of that theoretically possible, and this led to a careful examination of the acid solution which had been separated from the neutral substance by filtration. On the addition of ammonia, a caseous precipitate separated, which soon hardened, and when rubbed with methyl alcohol this yielded a sparingly soluble substance (a), which was collected and washed with a little methyl alcohol to remove a readily soluble substance (b). The

G G* 2

substance (a) on fractional crystallisation from methyl alcohol was separated into a small quantity of a new base (m. p. 168—170°) and a considerable quantity (0·8 gram) of unreduced ψ-dihydro-methyl*iso*anhydrocryptopine (m. p. 140°). In view of the fact that reduction had been carried out at the boiling point and with a very large excess of amalgam, it is remarkable that so much of this base should have remained unreduced. The base melting at 168—170° is very sparingly soluble in boiling methyl alcohol, from which it separates as a voluminous mass of colourless needles. The solution in acetic acid is coloured yellowish-brown by sulphuric acid, and the addition of a drop of dilute nitric acid changes the colour to brownish-pink:

0·1077 gave 0·2853 CO_2 and 0·0662 H_2O.   C = 72·1; H = 6·8.

$C_{22}H_{25}O_4N$ requires C = 71·9; H = 6·8 per cent.

This analysis shows that the base is isomeric with dihydro-methyl*iso*anhydrocryptopine (m. p. 122°) and ψ-dihydromethyl*iso*-anhydrocryptopine (m. p. 140°), but no evidence is available to explain this isomerism.

The methyl-alcoholic filtrate from the substance (b) was mixed with much ether, the ethereal solution washed until quite free from methyl alcohol, dried over potassium carbonate, concentrated, and left in the ice-chest for a week, during which it deposited a small crop of the base melting at 140°, which is practically insoluble in ether.

As no further separation took place on allowing the ether to evaporate in the ice-chest, the base was dissolved in dilute hydrochloric acid and precipitated with ammonia, when a caseous mass separated which, after drying over phosphoric oxide in a vacuum desiccator, gave numbers indicating that the base is *tetrahydro-methyliso anhydrocryptopine,*

$$CH_3$$
$$\backslash\!\!-CH\!-\!CH\ Me$$
$$\backslash\!-----CH\cdot NMe_2$$
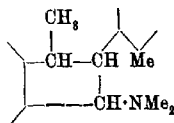
0·1139 gave 0·2969 CO_2 and 0·0753 H_2O.   C = 71·0; H = 7·5.

$C_{22}H_{27}O_4N$ requires C = 71·5; H = 7·3 per cent.

This base is very readily soluble in the usual solvents, and all attempts to obtain it in a crystalline condition were unsuccessful. The solution in benzene becomes hot on the addition of methyl sulphate, clouds, and a syrup separates which hardens when rubbed with ether. This methosulphate, which is very readily soluble in

water or methyl alcohol, yields a heavy syrup on the addition of boiling potassium iodide to its hot aqueous solution. On remaining in the ice-chest, this gradually deposited nodular crystals, and, when rubbed with methyl alcohol, a considerable quantity of a white, crystalline substance separated, which was collected and recrystallised from methyl alcohol.

Tetrahydromethylisoanhydrocryptopine methiodide melts without effervescence at about 188—190° to a viscid, pale yellow syrup, is comparatively readily soluble in boiling methyl alcohol, but very sparingly so in the cold, and separates well as a glistening mass consisting of thin, flat plates with square ends:

0·1201 gave 0·2390 CO_2 and 0·0641 H_2O.   C = 54·3; H = 6·0.
   $C_{22}H_{27}O_4N,MeI$ requires C = 54·0; H = 5·8 per cent.

iso*Cryptopidene* (*B*) (m. p. 108°).—This substance is obtained when the methosulphate of dihydromethylisoanhydrocryptopine (3 grams) (p. 783), dissolved in boiling water (150 c.c.), is treated with sodium amalgam (150 grams of 3 per cent.), care being taken to keep the whole boiling during the operation. Immediately the amalgam is added, a syrupy substance begins to separate, and, if the mass is vigorously stirred, the reduction is finished in a few minutes. The syrupy substance, which crystallises on cooling, is collected and recrystallised from alcohol:

0·1291 gave 0·3497 CO_2 and 0·0701 H_2O.   C = 73·9; H = 6·1.
   $C_{20}H_{20}O_4$ requires C = 74·1; H = 6·2 per cent.

iso*Cryptopidene* (*B*) melts at 108°, is more readily soluble in methyl or ethyl alcohol than the modification (*A*), and separates in groups of glistening needles. It is readily soluble in benzene or acetone in the cold, or in boiling glacial acetic acid, and crystallises particularly well from 70 per cent. acetic acid as a voluminous mass of needles. The solution of a trace in glacial acetic acid gives with sulphuric acid a deep orange-red coloration, which becomes redder on the addition of a drop of dilute nitric acid.

Oxidation.—The solution of the substance (3 grams) in acetone (200 c.c.) is slowly oxidised by the addition of very finely powdered permanganate (5 grams) at the ordinary temperature, the operation requiring about five hours. The manganese precipitate was collected, washed with acetone, extracted with boiling water, and the brown extract concentrated and acidified, when an ochreous precipitate separated in quantity, and was washed and left in contact with porous porcelain until dry. The whole was then dissolved in boiling methyl alcohol and allowed to remain in the ice-chest for two days, when a crystalline acid (0·25 gram) had

separated; this was recrystallised from methyl alcohol, in which it is very sparingly soluble:

0·1060 gave 0·2391 CO_2 and 0·0460 H_2O.   C=61·5; H=4·9.

$C_{20}H_{20}O_8$ requires C=61·5; H=5·1 per cent.

This acid, which may be called *ketohydroxydihydro*isocryptopidenic *acid*, and the possible constitution of which is discussed on p. 734, is a colourless, satiny mass; it becomes salmon-coloured at 220° and melts at 227° without effervescence.

The solution in concentrated methyl-alcoholic potassium hydroxide becomes pink on boiling, and the colour gradually fades in contact with air.

A trace dissolved in a drop of acetic acid gives with sulphuric acid a deep brown coloration which, on the addition of a drop of dilute nitric acid, gradually fades. The methyl-alcoholic mother liquors of this acid contain a considerable quantity of readily soluble acids, and the acetone extract from the oxidation yields, on evaporation, a small quantity of a yellow syrup, but no attempt was made to identify these mixtures of substances.

The considerable quantities of cryptopine required for this investigation were collected for me by Messrs. T. and H. Smith, of Edinburgh, and I wish again to thank the firm and the managing director, Dr. Alexander Dey, for the generous assistance they have extended to me throughout this inquiry. I am also indebted to Mr. T. V. Barker and Miss M. V. Porter for undertaking the crystallographic measurement of some of the new derivatives. The analyses were again carried out by Mr. Fred Hall with characteristic skill.

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LXI.—*The Freezing Point of Solutions, with Special Reference to Solutions Containing Several Solutes.*

By CHARLES EDWARD FAWSITT.

IN proceeding to use freezing-point determinations for the estimation of certain ingredients in liquids containing an unlimited number of ingredients, the author found that it was necessary to consider rather closely the freezing points of solutions. In particular, for the purpose in question, it was necessary to consider

how the calculated molecular depression of the freezing point of a solvent by a solute is dependent on the concentration of the solute (Part I), and it was necessary further to consider what effect is produced on the freezing point of a solvent by several solutes used together, as compared with the effect of these solutes used separately (Part II).

These two matters are considered in this paper.

PART I.

The Effect of Concentration of Solute in Freezing-point Determinations.

The freezing point of a solvent is usually lowered by dissolving any substance in it, and for very dilute solutions the depression of the freezing point, (Δ), is proportional to n/N, where n is the number of solute molecules and N is the number of solvent molecules.

This proportionality is proved from theoretical considerations, but holds only for excessively dilute solutions. For solutions of a concentration of, say, 1—10 per cent. of solute, Δ is not strictly proportional to n/N, and it has been suggested that the formula

$$\Delta \propto \frac{n}{N+n}$$

should be used instead of

$$\Delta \propto \frac{n}{N}.$$

Taking the first formula, which is more commonly used,

Let $w =$ weight in grams of solute,
$\quad m =$ molecular weight of solute,
$\quad W =$ weight of solvent in grams,
$\quad M =$ molecular weight of solvent,

$$\Delta \propto \frac{w}{m} \times \frac{M}{W},$$

or

$$\Delta = K \times 1000 \times \frac{w}{m} \times \frac{1}{W} \quad . \quad . \quad . \quad . \quad (1)$$

where K is a constant (the van't Hoff constant) for the solvent and represents the depression caused by introducing one gram-molecular weight of solute into 1000 grams of solvent.

Equation (1) is usually employed in making freezing-point calculations, more especially where these are used in determining molecular weights of solutes.

It is observed that when the depressions Δ_1, Δ_2, Δ_3, corresponding with several weights of solute, w_1, w_2, w_3, are determined, the molecular weight of the solute, calculated according to equation (1), is often not constant, even with non-associated or non-dissociated solutes. In such cases, the numbers more often tend to rise than to fall.

It might be thought that by using the formula

$$\Delta \propto \frac{n}{N+n}$$

instead of

$$\Delta \propto \frac{n}{N},$$

better results would be obtained.

Now

$$\Delta \propto \frac{n}{N+n}$$

leads to

$$\Delta \propto \frac{M \cdot w}{[m \cdot W + wM]},$$

or

$$\Delta = K \times 1000 \cdot \frac{w}{m[W + w/m \cdot M]} \quad \cdots \quad (2)$$

where K is the same constant as in (1). The application of equation (2) to the calculation of molecular weights instead of (1) is not attended by satisfactory results.

In particular, it cannot be made to serve any useful purpose when the molecular weights, calculated according to (1), decrease as the concentration rises, a case which sometimes occurs.

If, however, instead of the expression in (2) we use the formula

$$\Delta = \frac{K \times 1000 \times w}{m[W + bw]} \cdot \quad \cdots \quad (3)$$

where b is an arbitrarily introduced constant dependent on solute and solvent, not necessarily equal to M/m, and, indeed, sometimes negative, the results obtained are satisfactory.

Abegg (*Zeitsch. physikal. Chem.*, 1894, **15**, 209) tried the equation

$$\Delta = \frac{K \times n \times 1000}{W} + B\left(\frac{n}{W}\right)^2 \quad \cdots \quad (4)$$

where K is the ordinary van't Hoff constant as used in equation (1), and should be the same for all solutes in any particular solvent, whilst B is an arbitrary constant which varies with the solute. The application of this formula (4) certainly gives better results

in many cases than (1) or (2), but is not so simple a formula as (3). The latter gives quite as good results as (4) both for solutions containing a single solute and solutions containing several solutes.

The author considers that formula (3) is the most suitable for adoption in freezing-point calculations.

The constant b in equation (3) can be calculated from two observations; if w_1 and w_2 be two different weights of a solute giving depressions Δ_1 and Δ_2 with a particular solvent, then

$$b = \frac{W(\Delta_1/w_1 - \Delta_2/w_2)}{\Delta_2 - \Delta_1}.$$

The constant B in equation (4) can also be calculated from two observations,

$$B = \frac{W^2(\Delta_1/w_1 - \Delta_2/w_2)}{w_1 - w_2}.$$

In the following tables, m is the (theoretical) molecular weight, m' is the molecular weight as calculated by the equation

$$m' = \frac{K \cdot 1000 \cdot w}{\Delta \cdot W} \quad \cdots \cdots (5)$$

m'' is the molecular weight as calculated by the equation

$$m'' = \frac{K \cdot 1000 \cdot w}{\Delta \cdot [W + bw]} \quad \cdots \cdots (6)$$

m''' is the molecular weight as calculated by the equation

$$m''' = \frac{K \cdot 1000 \cdot w}{W[\Delta - B \cdot w^2/W^2]} \quad \cdots \cdots (7)$$

which is derived from equation (4).

From tables I, II, III, and IV it will be seen that m'' is fairly constant whether m' rises or falls with increasing concentration of solute.

In table II, m''' is also given, and it will be seen that it is just as constant as m'', but not more so.

TABLE I.

Solute, *Ethyl Ether*, $m = 74$; Solvent, *Cineole*.
$W = 18 \cdot 27$, $b = 1 \cdot 53$, $K = 6 \cdot 7$.

Grams of solute in 100 grams of solvent.	Δ.	m' (calculated).	m''.
0·707	0·624	76·0	75·1
1·48	1·275	77·6	75·9
2·2	1·875	78·5	76·0
3·4	2·874	79·3	75·2
5·15	4·255	81·0	75·1

TABLE II.

Solute, 1-α-*Phellandrene*, $m = 136$; *Solvent, Benzene.*
$B = -33.6$, $W = 18.47$, $b = 0.87$, $K = 5.0$.

$w \times 100/W$.	Δ.	m'.	m''.	m'''.
0.96	0.356	135.2	133.9	133.9
2.12	0.778	136.5	133.9	133.7
3.32	1.194	138.9	134.9	134.6
4.7	1.685	140.4	134.7	134.3
6.24	2.209	141.2	133.8	133.1
7.34	2.559	143.3	134.7	133.8

The variations in m'' (and m''') of the tables are not greater than the experimental errors.

Tables of this kind could be multiplied indefinitely.

Tables III and IV give examples where b has a negative value (that is, where the molecular weight as calculated from equation (1) falls with increasing concentration). Table III has been calculated from data given by Abegg (*loc. cit.*).

TABLE III.

Solute, *Ethyl Alcohol; Solvent,*
Water.
$K = 1.86$, $W = 100$, $m = 46$,
$b = -0.5$.

TABLE IV.

Solute, *Sucrose; Solvent, Water.*
$K = 1.86$, $W = 100$, $m = 342$,
$b = -0.26$.

w.	Δ.	m'	m''	w.	Δ.	m'	m''
8.10	3.215	46.8	48.8	0.973	0.053	341.4	342.3
10.75	4.35	46.0	48.6	2.231	0.123	337.4	339.3
13.81	5.605	45.8	49.2	4.276	0.237	335.6	339.4
17.79	7.49	44.6	49.2	8.550	0.481	330.7	338.2
22.50	9.705	43.1	48.5	17.292	0.989	325.1	340.2
32.68	15.09	40.2	48.1				

In table III it will be seen that m'' is constant within the experimental error up to a concentration of 32·68 per cent. of solute. Table IV is calculated from data given by Raoult (1898).

When the molecular weight as calculated according to equation (5) rises with increasing concentration, this is due probably (i) to the volume of the solution becoming continually greater than the volume of the solvent, or (ii) to association of the solute molecules.

When the molecular weight as calculated according to (5) falls with increasing concentration, this is due probably to combination between solute and solvent.

Whatever be the cause of the rising or falling of the calculated molecular weight, there seems to be little doubt that where the molecular weight calculated according to (5) rises or falls with

change of concentration, formula (6) gives values for m'' constant to about 1 per cent. This is, then, the calculated value of the molecular weight for very small concentrations. It does not immediately follow that this constant value (m'') represents accurately the true molecular weight (m), for there are other abnormalities noticed in the results of freezing-point measurements besides the rising and falling of the (calculated) molecular weight. The molecular weight as calculated for small concentrations may be higher or lower than the true molecular weight. It is higher in the case of many solutes showing association, for example, ethyl alcohol dissolved in cineole. It is also sometimes lower than the true molecular weight; this is more particularly noticeable in the case of some terpenes dissolved in benzene and in cineole.

PART II.

Freezing Point of a Mixture of Solutes Dissolved in a Solvent.

In proceeding to the case of several solutes dissolved together in a solvent, it will be desirable to eliminate certain complications. For example, it is not desirable to use as solutes in the mixture, (i) such solutes as exhibit association or dissociation in solution, (ii) such as will form mixed crystals with the solvent, (iii) such as will combine with the solvent or with each other.

In some cases, a fairly close agreement is observed between the depression of the freezing point, caused by a mixture of solutes, and the sum of the depressions, caused by the ingredients when introduced by themselves (separately) into the solvent.

TABLE V.				TABLE VI.		
Solvent, Benzene; Solute, Toluene.				Solvent, Benzene; Solute, p-Xylene.		
$W = 18\cdot65$, $K = 5\cdot0$.				$W = 15\cdot092$, $K = 5\cdot0$.		
W	Percentage of solute.	Δ.		w	$w \times 100/W$.	Δ.
0·1822	0·98	0·542		0·2306	1·53	0·750
0·3522	1·89	1·017		0·5224	3·46	1·626
0·6866	3·68	2·028		0·8151	5·40	2·542

In table VII and the following tables, Δ_1 is the depression of the freezing point of a mixture of solutes in a solvent obtained by adding together the calculated depressions of the freezing point caused by each ingredient. Δ is the observed depression.

TABLE VII.

Solvent, Benzene; Solute, a Mixture containing 84·7 *per cent. of Toluene and* 15·3 *per cent. of* p-*Xylene.*

$$W = 15·29.$$

$w.$	$\Delta.$	$\Delta_1.$
0·1887	0·670	0·648
0·3663	1·274	1·268
0·615	2·114	2·139

The calculated and observed depressions do not differ by much more than the experimental errors in this case.

However, if a considerable number of cases are examined, using various solutes and solvents, it will be found that there is often a considerable discrepancy between the values of Δ and Δ_1, especially at large concentrations; sometimes Δ is greater than Δ_1, sometimes less. This is, however, only to be expected from equation (3).

From equation (3) we are led to believe that, instead of using W, the weight of pure solvent, in our calculations, we should use $W + bw$.

Consider now two solutes, P and Q, having molecular weights m_p and m_q; let w_p grams of P be dissolved in a solvent, giving a depression Δ_p; let w_q grams of Q when dissolved (separately) in the solvent give a depression Δ_q.

Then the separate depressions are:

$$\Delta_p = \frac{K.1000.w_p}{m_p.[W + b_p w_p]} \quad \text{and} \quad \Delta_q = \frac{K.1000.w_q}{m_q[W + b_q w_q]},$$

and the sum

$$\Delta_p + \Delta_q = K.1000 \left\{ \frac{w_p/m_p}{[W + b_p w_p]} + \frac{w_q/m_q}{[W + b_q w_q]} \right\} \quad . \quad (8)$$

The sum $\Delta_p + \Delta_q$ differs from the observed value Δ_{p+q}, since the observed value would be expected to be given by

$$\Delta_{p+q} = \frac{K.1000\{w_p/m_p + w_q/m_q\}}{[W + b_p w_p + b_q w_q]} \quad . \quad . \quad . \quad (9)$$

If b_p and b_q are positive, then Δ_{p+q} will be less than $\Delta_p + \Delta_q$. If b_p and b_q are negative, then Δ_{p+q} will be greater than $\Delta_p + \Delta_q$. We may say then, in general, that on mixing two solutes the molecular weights of which when calculated according to the usual formula (equation 5) rise with increasing concentration $(b+w)$, we should expect that the actual depression produced by the two

together would be less than the sum of the depressions produced by each solute separately.

If, on the other hand, the molecular weights when calculated according to equation (5) decrease with increasing concentration (*b* negative), we should expect that the depression produced by two solutes together would be greater than the sum of the depressions of the separate solutes.

An examination of a considerable number of cases shows that, qualitatively, these statements are borne out by facts.

It is assumed, of course, in such cases that there is no combination between the various solutes. This would itself have the effect of making the observed less than the calculated depression.

Below are given the results of a number of freezing-point determinations on single solutes in benzene showing how the molecular weight, calculated according to equation (5), alters with change of concentration, and, subsequently, tables showing the results obtained from mixtures of some of these solutes in benzene.

Results for mixtures of solutes are given for the three solvents benzene, nitrobenzene, and water.

Δ_2 in the following tables denotes the calculated depression as obtained from equation (9).

m^l is calculated from equation (5).

Percentage of solute means weight of solute in 100 grams of solvent.

Benzene as Solvent.

The following results were obtained with individual solutes.

TABLE VIII.			TABLE IX.		
Solvent, Benzene; Solute, Toluene.			Solvent, Benzene; Solute, m-Xylene.		
$K=5$, $m=92$.			$m=106$.		
Percentage weight of solute.	Δ.	m'.	Percentage weight of solute.	Δ.	m'.
1·467	0·847	86·6	1·189	0·568	104·7
3·088	1·754	88·1	2·674	1·253	106·7
4·715	2·588	91·1	4·111	1·881	109·3
6·205	3·338	93·0	5·595	2·526	110·8
7·803	4·148	94·1	6·773	3·014	112·4

b Calculated from these figures is ·1·312.

b Calculated from these figures is 1·339.

TABLE X.

Solvent, Benzene; Solute, d-Pinene.

$m = 136.$

Percentage.	Δ.	m .
1·411	0·54	130·6
2·823	1·032	136·9
4·438	1·564	141·9
6·193	2·15	144·1

b Calculated from observations (1) and (4) is 2·21.

TABLE XI.

Solvent, Benzene; Solute, α-Phellandrene.

$m = 136.$

Percentage.	Δ.	m'.
0·962	0·356	135·2
2·123	0·778	136·5
3·316	1·194	138·9
4·731	1·685	140·4
6·236	2·209	141·2
7·335	2·559	143·3

b Calculated from observations (1) and (6) is 0·87.

TABLE XII.

Solvent, Benzene; Solute, Cineole.

$m = 154.$

Percentage.	Δ.	m'.
1·046	0·350	149·4
2·708	0·870	155·7

b Calculated from observations (1) and (2) is 2·59.

TABLE XIII.

Freezing-point Determinations with more than One Solute in Benzene as Solvent. Solvent, Benzene (K = 5·0).

No.	Solute.	Value of " b " for solute.	Percentage weight of solute.	Δ.	Δ₁.	Δ₂.	Percentage difference between Δ and Δ₂.
1	Toluene	1·312	2·368	1·569	1·604	1·588	1·2
	m-Xylene	1·339	0·532				
2	Toluene	1·312	3·759	2·469	2·508	2·466	− 0·1
	m-Xylene	1·339	0·845				
3	Toluene	1·312	4·764	3·299	3·442	3·334	1·1
	m-Xylene	1·339	1·708				
4	Cineole	2·59	4·107	1·881	2·047	1·930	2·7
	d-Pinene	2·21	1·068				
	Phellandrene	0·87	0·944				
5	Cineole	2·59	1·571	1·832	1·943	1·824	−0·5
	d-Pinene	2·21	2·025				
	Phellandrene	0·87	1·790				

Nitrobenzene as Solvent.

Nitrobenzene is similar as a solvent to benzene in that the value of *b* for solutes in nitrobenzene was positive in all cases experi-

mented on. The molecular weight (m') of single solutes dissolved in nitrobenzene, if calculated according to equation (5), rises with increasing concentration. The results for the individual solutes are omitted here, but the results for several solutes dissolved together in nitrobenzene are given in table XIV.

As in the case of benzene, the sum of the individual depressions is always greater than the depressions obtained for the solutes when dissolved together.

The corrected calculated value (Δ_2), using the b correction as per equation (9), is, however, as with benzene, much nearer to the observed value.

TABLE XIV.

Freezing-point Determinations with more than One Solute in a Common Solvent. Solvent, Nitrobenzene $(K = 7\cdot0)$.

No.	Solute.	Value of " b " for solute.	Percentage weight of each solute.	Δ.	Δ_1.	Δ_2.	Percentage difference between Δ and Δ_2.
1	Toluene......	2·295	0·926	2·439	2·534	2·463	+1
	Benzene ...	2·36	2·048				
2	Toluene ...	2·295	1·624	4·070	4·314	4·117	+1·1
	Benzene ...	2·36	3·587				
3	Toluene......	2·295	2·401	2·800	2·929	2·820	+0·7
	m-Xylene	1·138	0·861				
	Benzene ...	2·36	0·591				
4	Toluene......	2·295	3·919	4·323	4·671	4·399	+1·7
	m-Xylene ...	1·138	1·404				
	Benzene ...	2·36	0·964				
5	Toluene......	2·295	2·574	3·599	3·883	3·672	+2·0
	m-Xylene ...	1·138	0·578				
	Benzene ...	2·36	1·750				

Water as Solvent.

In this case, it was not thought necessary to carry out any experimental work, as sufficient material for calculation may be obtained in the literature dealing with freezing points.

Using Abegg's numbers (*loc. cit.*), it is found that b is sometimes negative for solutes in aqueous solutions.

The values for b have been calculated for a number of solutes, and the results in table XV give the observed and calculated values for mixtures of these solutes.

TABLE XV.

Freezing-point Determinations with more than One Solute in a Common Solvent. Solvent, Water.

No.	Solute.	Value of "b" for solute.	Percentage weight of solute.	Δ.	Δ$_1$.	Δ$_2$.	Percentage difference between Δ and Δ$_2$.
1	Glycerol ...	−0·284	5·235	2·145	2·057	2·119	−1·3
	Sucrose ...	−0·24	16·857				
2	Glycerol ...	−0·284	10·90	3·48	3·294	3·431	−1·4
	Sucrose ...	−0·24	17·54				
3	Alcohol ...	−0·463	3·924	3·47	3·320	3·395	−2·1
	Glycerol ...	−0·284	8·64				
4	Alcohol ...	−0·463	5·474	4·13	4·058	4·074	−1·4
	Acetone......	0·235	6·251				
5	Alcohol	−0·463	5·934	6·55	6·393	6·437	−1·7
	Acetone......	0·235	13·555				

It will be noticed that for the solutes and solvents considered, and in spite of the corrected method of calculation employed when several solutes are used together, an error of as much as 2 per cent. occurs in some cases. This error is sometimes positive and sometimes negative, and may be due, (i) to reaction between the various solutes, or (ii) to action of the solute on the solvent, or (iii) to experimental errors in determining the freezing point of the solutions.

When freezing-point determinations are to be used for purposes of analysis, these errors have to be taken into account. Before the method can be applied directly to a given sample, the errors of determination must have been ascertained by experiments on somewhat similar material.

Summary.

(1) In freezing-point determinations, there may with advantage be substituted for W, the weight of solvent, the expression $W + bw$, where w is the weight of the solute and b is a constant which depends both on the solute and the solvent, and is at present determinable only by experiment with the solute and solvent.

(2) When several solutes are dissolved at one time in the same solvent, then, if b is positive for the individual solutes, the sum of the individual depressions of the freezing point by the various solutes is greater than the observed depression of the freezing point; if b is negative for each individual solute, the sum of the

individual depressions is less than the observed depression of the freezing point.

(3) If several solutes are dissolved together in a solvent and the quantity of solvent be taken as $W + w_1b_1 + w_2b_2 + w_3b_3 +$, where W is the actual weight of the solvent, and w_1, w_2, w_3 are the weights of the solutes, and b_1, b_2, b_3 are the values of the constant b for each solute, as explained in paragraph (1) above, then the sum of the calculated values of the depressions of the individual solutes differs from the observed total depressions by only a small error in all cases considered by the author.

I desire to thank Mr. C. H. Fischer for carrying out the experimental work described in this paper.

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LXII.—*The Use of Freezing-point Determinations in Quantitative Analysis.*

By CHARLES EDWARD FAWSITT.

CONSIDERABLE use has been made of freezing-point determinations as an aid to analytical work in recent years.

The freezing point of a liquid like milk or blood serum has been used as a characteristic for these substances independently of what the constituent solutes are.

Fox and Barker (*J. Soc. Chem. Ind.*, 1917, **36**, 842) have made use of a determination of the freezing point to obtain the percentage of phenol in commercial cresylic acid. There is a little uncertainty in using the freezing-point results in such a case, because the other substances in crude cresylic acid, namely, the three cresols, have all the same molecular weight.

Weiss and Downs (*ibid.*, 863) show that the percentage of phenol in tar oils may be determined by a freezing-point determination provided a density determination of the mixture is also carried out.

Drapier (*Compt. rend.*, 1915, **161**, 461) has suggested that the percentage of one ingredient A_1 in a mixture A could be obtained provided that one knows the lowering of the freezing point by the mixture A (solute) when dissolved in A_1 (solvent), and also when A is dissolved in some other solvent, S, which is not an ingredient of A. Drapier, however, has apparently not followed up this

suggestion by publishing any experimental support for the method. It seemed to the author, however, that this method was worth while investigating.

Theoretical.—Let us suppose that the depression of freezing point produced by dissolving a solute in a solvent is (1) proportional to the concentration of the solute, (2) inversely proportional to the molecular weight of the solute if equal weights of different solutes are compared; let us suppose, further, (3) that a solute exercises its usual effect in depressing the freezing point of a solvent independently of the presence or absence of other solutes.

Conditions (1) and (2) are approximately true for most dilute solutions. The effect of one solute on the depression of the freezing point of a solvent, when another second solute is present (3), has not yet been very thoroughly investigated, but in several investigated cases (3) certainly does not hold quite true even in dilute solution (see preceding paper). In developing the theory of this process it will, however, be assumed in the first instance that (1), (2), and (3) hold good. Consider a liquid mixture A. The mixture A is made up of several ingredients, A_1, A_2, A_3, A_4, etc. . . . A_n. It is required to find out the percentage of the ingredient A_1. The ingredient A_1 must be such that it is capable of being frozen at a convenient temperature.

Obtain also a solvent, S, in which A is completely soluble; S must also be a substance (liquid) which can be frozen at a convenient temperature.

A small quantity, a, of the substance A is dissolved in P grams of the solvent S, and the depression in the freezing point of S noted. Call this Δ_s. Also a quantity of the mixture A, say b grams, is dissolved in Q grams of the solvent A_1, and the depression in the freezing point of $A_1 = \Delta_{A_1}$ noted.

Further, let $a = a_1 + a_2 + a_3 + a_4$ . . ., where a_1, a_2, etc., are the weights of the several ingredients A_1, A_2, etc., in a; let $b = b_1 + b_2 + b_3 + b_4$ . . ., where b_1, b_2, etc., are the weights of the ingredients A_1, A_2, etc., in b; let $K_1 =$ the cryoscopic constant for the solvent, S, that is, the depression produced in the freezing point of S by dissolving in 1000 grams of S one gram-molecular weight of any solute; let $K_2 =$ the cryoscopic constant for the solvent A_1; let m_1, m_2, m_3 . . . be the molecular weights of the constituents A_1, A_2, A_3 . . . ., then

$$\Delta_s = \frac{1000 \; K_1}{P} \left(\frac{a_1}{m_1} + \frac{a_2}{m_2} + \frac{a_3}{m_3} + \ldots \right) \quad . \quad . \quad (1)$$

and

$$\Delta_{A_1} = \frac{1000 \; K_2}{Q + b_1} \left(\frac{b_2}{m_2} + \frac{b_3}{m_3} + \ldots \right) \quad . \quad . \quad (2)$$

Now if $a/b = r$, (2) becomes

$$\Delta_{A_1} = \frac{1000\, K_2}{(Q+b_1)r} \cdot \left(\frac{a_2}{m_2} + \frac{a_3}{m_3} + \ldots \right) \quad . \quad (3)$$

Multiplying equation (1) by $\dfrac{K_2}{(Q+b_1)r}$, and (3) by $\dfrac{K_1}{P}$, we get

$$\frac{K_2\Delta_s}{(Q+b_1)r} - \frac{K_1\Delta_{A_1}}{P} = \frac{K_1 K_2 \times 1000}{P\cdot(Q+b_1)\cdot r} \cdot \frac{a_1}{m_1}$$

$$\therefore a_1 = \frac{m_1(K_2\Delta_s P - K_1\Delta_{A_1}rQ)}{K_1(1000\ K_2 + m_1\Delta_{A_1})} \quad . \quad . \quad . \quad (4)$$

It has, however, been pointed out (see preceding paper) that in dealing with ordinary concentrations, the weights of solvent should not be taken as P and $(Q + b_1)$, but that these values should be corrected by the addition of a term depending on the weight of solute present. P would then become

$$P + \delta_1 a_1 + \delta_2 a_2 + \delta_3 a_3 + \delta_4 a_4 + \ldots,$$

where δ_1, δ_2, δ_3 . . . are constants for each ingredient of the solute $= P + \delta a$, where δ is the average value of the constants $\delta_1, \delta_2, \delta_3, \delta_4$ for the several ingredients of the solute A. Similarly, $Q + b_1$ would become $Q + b_1 + \gamma(b_2 + b_3 + b_4 + \ldots)$, where γ is the average value of the correction factor for the solutes A_2, A_3, A_4, A_5, etc.

Formula (4) then becomes

$$a_1 = \frac{m_1[K_2\Delta_s(P + \delta a) - K_1\Delta_{A_1}\{Q + \gamma(b - b_1)\}r]}{K_1(1000\ K_2 + m_1\Delta_{A_1})} \quad . \quad (5)$$

It may be wondered how the value for b_1 can be obtained for insertion in this formula (5). To obtain this, a calculation of a_1 is first made, using formula (4). Then $b_1 = a_1/r$. This value, which is only roughly, but yet sufficiently, accurate is used for a more accurate determination of a_1, according to equation (5).

The values of δ and γ can be obtained directly from the experiment used in determining a_1.

In many cases it will be necessary to introduce a further correction in the formula. It has already been pointed out in the preceding paper that the depression of freezing points caused by a number of solutes in one solvent is somewhat different from the expected value even after due allowance has been made by the correction in the amount of solvent as used in obtaining equation (5) from equation (4).

The values of Δ_s and Δ_{A_1} should, then, be corrected further by an amount which can only be determined by previous experiment on the class of solute which is under investigation.

Let us use the correction factors (constants) U and V for Δ_t and Δ_{A_1}.

The percentage of A_1 in A is then

$$\frac{100 . m_1[K_2\Delta_s U(P+\delta a) - K_1\Delta_{A_1}\{Q+\gamma(b-b_1)\}r . V]}{a . K_1[1000K_2+\Delta_{A_1}m_1]} \quad (6)$$

Another correction which must sometimes be introduced is due to the fact that when A_1 is dissolved in the solvent S, the calculated molecular weight may not be exactly m_1, but some other value, say m'_1. This value, if appreciably different from m_1, should be substituted for m_1. The formula to be used is then: percentage of

$$A_1 = \frac{100 . m_1[K_2\Delta_s U(P+\delta a) - K_1\Delta_{A_1}\{Q+\gamma(b-b_1)\}rV]}{aK_1[1000K_2+\Delta_{A_1}m'_1]} \quad (7)$$

In considering what estimations the method might usefully be applied to, the author thought that the determination of (a) benzene in light coal-tar oils was a suitable case, also (b) the determination of cineole in eucalyptus oils. With regard to (a), the determination of benzene can be obtained approximately (1) by distillation, (2) sometimes by direct determination of the freezing point, especially after addition of extra benzene, (3) by nitration, with subsequent determination of the products, but the method at present under discussion would sometimes be found more suitable.

With regard to the determination of cineole in eucalyptus oils, the phosphoric acid method, although fairly satisfactory as a rule, requires a comparatively large quantity of oil (10 grams). The resorcinol method has been used a good deal lately by H. G. Smith, but he has informed the author that in certain cases it is not trustworthy.

In the following experiments, as ordinary "Beckmann" type of thermometer graduated to 0·01° was used.

Estimation of Benzene in Mixtures.

The mixtures were used as solutes in depressing the freezing point of nitrobenzene and of benzene.

K_2 for benzene $= 5\cdot0$; K_1 for nitrobenzene $= 7\cdot0$.

The results were calculated according to the formula: percentage of benzene $=$

$$\frac{100 \times 78[5 . \Delta_s . (P+2\cdot3a) . 1\cdot018 - 7 . \Delta_{A_1} . \{Q+1\cdot4(b-b_1)\} . 1\cdot008 . r]}{a . 7 . [5000+\Delta_{A_1} . 78]}$$

Mixture A.

The composition of the mixture was: benzene 68·85, toluene 31·15 per cent.

TABLE I.

Freezing-point Determinations in Nitrobenzene as Solvent.

No.	Percentage of solute.	Δ_f.
1	1·010	0·86
2	2·159	1·819
3	2·974	2·439
4	4·070	3·266
5	5·211	4·07

TABLE II.

Solvent, Benzene.

No.	Percentage of solute.	Δ_{f_1}.
1	1·580	0·30
2	3·941	0·702
3	6·541	1·130
4	9·22	1·550
5	11·88	1·920

TABLE III.

Calculation of Percentage of Benzene in Mixture A.

Observations used.		Percentage calculated.
Table I.	Table II.	
No. 1	No. 2	69·6
3	3	70·2
5	5	70·4

Mixture B.

The composition of the mixture was: benzene 15·3, toluene 62·4, m-xylene 22·3 per cent.

TABLE IV.

Solvent, Nitrobenzene.

No.	Percentage of solute.	Δ_f.
1	1·383	1·040
2	2·589	1·909
3	3·853	2·800
4	5·273	3·691
5	6·287	4·323

TABLE V.

Solvent, Benzene.

No.	Percentage.	Δ_{f_1}.
1	1·392	0·642
2	3·131	1·438
3	4·844	2·169
4	6·409	2·789
5	7·734	3·299

TABLE VI.

Calculation of Percentage of Benzene in Mixture B.

Observations used.		Percentage calculated.
Table IV.	Table V.	
No. 1	No. 1	14·1
2	2	13·4
3	3	14·9
4	4	15·0

Mixture C.

The composition of the mixture was: benzene 10·00, toluene 61·48, *m*-xylene 9·19, o-xylene 8·56, *p*-xylene 9·06, thiophen 1·71 per 'cent.

<table>
<tr><td colspan="3">TABLE VII.</td><td colspan="3"></td></tr>
<tr><td colspan="3">*Solvent, Nitrobenzene.*</td><td colspan="3">TABLE VIII.</td></tr>
<tr><td>No.</td><td>Percentage of solute.</td><td>Δ_s.</td><td>No.</td><td>Percentage of solute.</td><td>Δ_{A_1}.</td></tr>
<tr><td>1</td><td>1·193</td><td>0·898</td><td>1</td><td>1·488 '</td><td>0·737</td></tr>
<tr><td>2</td><td>2·302</td><td>1·684</td><td>2</td><td>2·925</td><td>1·417</td></tr>
<tr><td>3</td><td>3·627</td><td>2·577</td><td>3</td><td>4·248</td><td>1·980</td></tr>
</table>

TABLE IX.

Calculation of Percentage of Benzene in Mixture C.

Observations used.		Percentages
Table VII.	Table VIII.	calculated.
1	1	8·3
3	3	10·2

Estimation of Cineole in Mixtures.

The mixtures were made of cineole, pinene, and *l*-α-phellandrene. The mixtures were used as solutes in depressing the freezing points of benzene and of cineole.

K_1 for benzene $= 5·0$; K_2 for cineole $= 6·7$.

The results were calculated according to the formula: percentage of cineole $=$

$$\frac{100 \times 146[6\cdot7 \cdot 1\cdot02 \cdot \Delta_s \cdot (100 + 1\cdot7a) - 5\cdot0 \times 1\cdot04 \cdot \Delta_{A_1} \cdot \{100 + 1\cdot7(b - b_1)r\}]}{a \cdot 5[6700 + \Delta_{A_1} \cdot 146]}$$

It will be noticed that 146 (obtained by experiment) was used for the molecular weight of cineole in benzene, instead of 154, the theoretical value.

Mixture D.

The composition of the mixture was: cineole 67·1, pinene 17·5, phellandrene 15·4 per cent.

<table>
<tr><td colspan="3">TABLE X.</td><td colspan="3">TABLE XI.</td></tr>
<tr><td colspan="3">*Solvent, Benzene.*</td><td colspan="3">*Solvent, Cineole.*</td></tr>
<tr><td>No.</td><td>Percentage of solute.</td><td>Δ_s.</td><td>No.</td><td>Percentage of solute.</td><td>Δ_{A_1}.</td></tr>
<tr><td>1</td><td>1·887</td><td>0·642</td><td>1</td><td>3·59</td><td>0·568</td></tr>
<tr><td>2</td><td>3·948</td><td>1·313</td><td>2</td><td>8·20</td><td>1·262</td></tr>
<tr><td>3</td><td>5·759</td><td>1·881</td><td>3</td><td>13·72</td><td>2·051</td></tr>
</table>

TABLE XII.

Calculation of Percentage of Cineole in Mixture D.

Observations used.		Percentage
Table X.	Table XI.	calculated.
1	1	67·2
2	2	68·5
3	3	67·8

Mixture E.

The composition of the mixture was: cineole 29·2, pinene 37·6, phellandrene 33·2 per cent.

TABLE XIII.	TABLE XIV.

Solvent, Benzene.			*Solvent, Cineole.*		
No.	Percentage of solute.	Δ_t.	No.	Percentage of solute.	Δ_{d_1}.
1	1·786	0·633	1	1·48	0·518
2	3·57	1·244	2	3·957	1·356
3	5·39	1·832	3	6·63	2·210

TABLE XV.

Calculation of Percentage of Cineole.

Observations used.		Percentage
Table XIII.	Table XIV.	calculated.
1	1	28·4
2	2	28·1
3	3	29·4

Mixture F.

The composition of the mixture was: cineole 54·3, pinene 24·3, phellandrene 21·4 per cent.

TABLE XVI.	TABLE XVII.

Solvent, Benzene.			*Solvent, Cineole.*		
No.	Percentage of solute.	Δ_t.	No.	Percentage of solute.	Δ_{d_1}.
1	1·708	0·599	1	2·124	0·479
2	3·596	1·219	2	7·580	1·655

TABLE XVIII.

Calculation of Percentage of Cineole in Mixture F.

Observations used.		Percentage
Table XVI.	Table XVII	calculated.
1	1	55·0
2	2	52·9

From these results, it will be seen that the calculation yields figures which are within about 2 units of the true percentage. This error is completely accounted for by errors of experiment, more particularly the reading of the thermometer. It is not possible to be sure that the calculated percentage is any nearer to the true result than this, using the Beckmann freezing-point apparatus in the ordinary way. As unknown mixtures might in some cases contain unknown ingredients, it would be impossible, unless with previous experience with similar mixtures, to know the values of U and V in equation (7), and any tentative value used for U or V might result in a rather large error in the calculated percentage. In certain cases of this kind experimented on, the error in the percentage was as high as 8 units. The error is stated above as so many units, because in the formula (7), for the calculation of the percentage of A_1, one term containing Δ_{A_1} is subtracted from another containing Δ_s, giving a number which varies directly as the final result (percentage of A_1). It is not therefore possible to express the error of experiment as a percentage.

Summary.

The method of estimating an ingredient A_1 in a substance A by finding the freezing-point depression of A in A_1 (as solvent), and also in some other solvent, S, may be applied in special cases where it is possible to experiment previously with samples of substance somewhat similar to A. The percentage of A_1 can then be determined in certain cases to an accuracy of about two units with the ordinary freezing-point apparatus.

When it is not possible to experiment with the same class of substance beforehand, the method of determination is liable to give a result with a much larger error. The method can therefore only be recommended when (1) there has been previous experience with the same class of substance, or (2) when other possible methods of determination are not capable of a greater degree of accuracy, or (3) where other methods require for their successful application a larger quantity of substance than is available. The freezing-point method already described requires for its successful application about 1 gram of substance, but it is more satisfactory if a larger amount, say 4—6 grams, is available.

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LXIII.—*The Constitution of the Disaccharides. Part III. Maltose.*

By WALTER NORMAN HAWORTH and GRACE CUMMING LEITCH.

MALTOSE is a reducing sugar which yields, on hydrolysis with dilute acid or with the enzyme maltase, two molecular proportions of glucose. Consequently, it is regarded as a biose having the reducing group of one glucose molecule united through an anhydride linking with a second glucose residue. Confirmation of this view is found in the oxidation of maltose to maltobionic acid, which gives rise on hydrolysis to glucose and gluconic acid (Fischer and Meyer, *Ber.*, 1889, **22**, 1941).

No evidence has hitherto been available indicating which of the hydroxyl groups of the second glucose residue is involved in this union (see formula I). The present authors have shown in Part II of this series of communications (T., 1918, **113**, 188) that in lactose the reducing group of the galactose residue is linked with the hydroxyl group of the penultimate carbon atom of the glucose molecule. The possibility that this mode of linking was present also in maltose appeared improbable in view of Hudson's observation (*J. Amer. Chem. Soc.*, 1916, **38**, 1566) that lactose exhibits a close parallelism with cellobiose and not with melibiose, to which a different constitution has been assigned (Haworth and Leitch, *loc. cit.*). There was, however, no definite ground for excluding this possibility in the case of maltose, nor, indeed, for assuming that any one hydroxyl group attached to the third, fifth, or sixth carbon atom from the reducing end of the second glucose chain could not equally well be concerned in the union of the two molecules of the hexose.

In the course of the present investigation, this uncertainty has been removed, and it has been shown that maltose must have the constitution indicated below, and thus corresponds structurally,

(I) Maltose.   Melibiose.
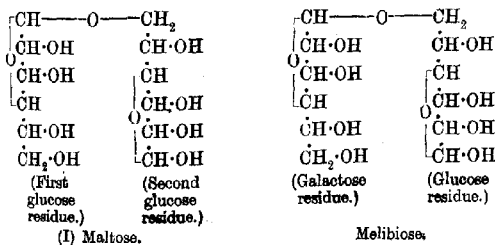
among the diglucose disaccharides, with melibiose of the glucose-galactose class.

This constitution assigned to maltose is identical with the current provisional formula which has found expression in recent text-books, and was proposed, along with alternative formulæ, by Fischer ("Untersuchungen über Kohlenhydrate und Fermente," 1884—1908, p. 92).

Following the general lines indicated in the previous research on lactose (*loc. cit.*), the methylation of maltose was effected by the agency of methyl sulphate and sodium hydroxide, and, as a precautionary measure designed to ensure that methylation was complete, the material isolated from this reaction was finally submitted to an alternative treatment with Purdie's reagent, namely, silver oxide and methyl iodide. Eight methyl groups were found to have been introduced into the maltose molecule, and heptamethyl methylmaltoside (VII), corresponding in the degree of substitution with the known octa-acetylmaltose, was isolated as a colourless gum, which distilled as a mobile syrup at 189—190°/0·09 mm. The compound was soluble in water and did not reduce Fehling's solution. It dissolved freely in methyl or ethyl alcohol or acetone, and showed $[\alpha]_D + 89\cdot6°$, the equilibrium value for maltose itself being 137·7°.

There can be little doubt, in view of other results obtained in methylating reducing sugars with methyl sulphate, that this substance is chiefly the β-form, containing also the stereochemical α-modification.

When heptamethyl methylmaltoside was hydrolysed with 5 per cent. aqueous hydrochloric acid for three hours at 85—100°, a mixture of tetramethyl and trimethyl glucoses was obtained as the product of cleavage. This was a mobile syrup, and the separation of the two constituents was effected by careful fractionation in the high vacuum of the Gaede pump. Two pure fractions, collected at 131°/0·3 mm. and at 171°/0·23 mm., were isolated along with the transition fraction distilling at temperatures intermediate between these limits. From the transition fraction, as will be shown later, more of the pure fractions was isolated. The first fraction, distilling at the lower temperature, crystallised immediately on nucleation with a crystal of tetramethyl glucose (VIII), and its complete identity with the latter substance was proved by determination of the melting point and also of that of a mixture with an authentic specimen of tetramethyl glucose. The specific rotation of the specimen derived from the hydrolysis of the methylated methylmaltoside was in agreement with the accepted,

equilibrium value, which is $[\alpha]_D +83°$. We can therefore confirm the similar observation made by Purdie and Irvine (T., 1905, **87**, 1029), who also isolated this compound from the product obtained by methylating maltose with silver oxide and methyl iodide.

The identification of the substance distilling at 171°/0·23 mm. presented greater difficulty. The analytical results were in agreement with the formula of a trimethyl glucose. It reduced Fehling's solution, and its comparative stability towards permanganate indicated that it was a reducing sugar of the butylene oxide type. It did not crystallise after nucleation with a specimen of the trimethyl glucose isolated from the hydrolysis of heptamethyl methyl-lactoside (Haworth and Leitch, *loc. cit.*), and failed to give an osazone with phenylhydrazine. Of the four formulæ possible for a trimethyl glucose of the butylene oxide type, those numbered III and V may for these reasons be excluded from immediate consideration.

⌈CH·OH	⌈CH·OH	⌈CH·OH	⌈C̶H·OH
O⌊ĊH·OMe	O⌊ĊH·OH	O⌊ĊH·OMe	O⌊CH·OMe
⌈ĊH·OMe	⌈ĊH·OMe	⌈ĊH·OH	⌈CH·OMe
⌊ĊH	⌊ĊH	⌊ĊH	⌊ĊH
ĊH·OMe	ĊH·OMe	ĊH·OMe	ĊH·OH
ĊH₂·OH	ĊH₂·OMe	ĊH₂·OMe	ĊH₂·OMe
(II.)	(III.)	(IV.)	(V.)
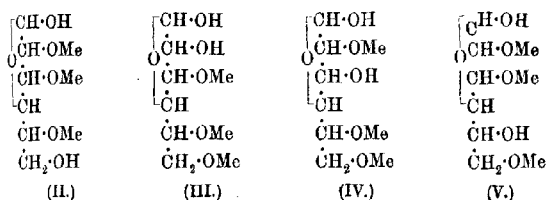
Moreover, it is clear from the presentation of these four possible formulæ that if proof could be found for the presence of a free primary alcohol group in the trimethyl glucose isolated during this investigation, this fact would definitely determine the constitution of the trimethyl hexose, as this terminal hydroxyl group is only present in formula II.

Accordingly, the trimethyl glucose was carefully oxidised with dilute nitric acid (D 1·2), and a liquid carboxylic acid was isolated which was shown also to be a lactone. On titration with $N/10$-alkali, an apparent neutral point was reached when rather less than one molecular proportion of alkali was introduced, and its behaviour on the subsequent addition of more alkali showed that a lactone ring was undergoing scission. Two molecular proportions of alkali were needed for complete neutralisation. The analytical data indicated that the lactonic acid had the molecular formula $C_9H_{14}O_7$, and contained three methoxyl groups. Its constitution can therefore only be represented by formula VI, and consequently the formula of the trimethyl glucose, from which by

oxidation the lactonic acid was obtained, is represented by formula II.

$$
\begin{array}{ccc}
\text{O}\left[\begin{array}{l} \text{CH·OH} \\ \overset{\bullet}{\text{CH·OMe}} \\ \text{CH·OMe} \\ \overset{\bullet}{\text{CH}} \end{array}\right. & & \text{O}\left[\begin{array}{l} \text{CO} \\ \overset{\bullet}{\text{CH·OMe}} \\ \text{CH·OMe} \\ \overset{\bullet}{\text{CH}} \end{array}\right. \\
\begin{array}{l} \overset{\bullet}{\text{CH·OMe}} \\ \overset{\bullet}{\text{CH}_2\text{·OH}} \end{array} & \xrightarrow{\text{Oxidation,}} & \begin{array}{l} \overset{\bullet}{\text{CH·OMe}} \\ \overset{\bullet}{\text{CO}_2\text{H}} \end{array} \\
\text{(II.)} & & \text{(VI.)}
\end{array}
$$
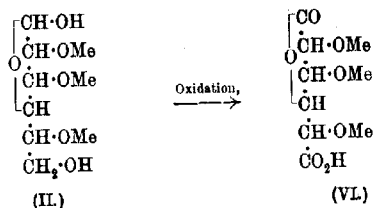
The product of oxidation is thus trimethyl saccharo-monolactone, and the primary alcohol group is shown to be present in the trimethyl glucose, since only such a group could undergo oxidation to a carboxyl group. This primary alcohol group has become exposed during the dissolution of partnership with the second methylated glucose residue occasioned by the hydrolysis of the biose.

The change in rotatory power, characteristic of lactones of the sugar series, was observed in the case of the lactonic acid. In aqueous solution, the value decreased from $[\alpha]_D + 78°$ to $+40°$ during four hours. In contact with a trace of hydrochloric acid, the value increased again to $+56°$.

A molecular weight determination in acetone solution by the ebullioscopic method gave the number 242, which is in fairly close agreement with that required (234) for the molecular formula $C_9H_{14}O_7$.

The behaviour of heptamethyl methylmaltoside (VII) on hydrolysis must therefore be formulated by the scheme outlined below, the dotted lines indicating the points of cleavage:

$$
\overset{\text{H}\,\text{OH}}{\underset{\text{OH}\,\text{H}}{
\text{O}\left[\begin{array}{l}
\text{CH}\!-\!-\!\text{O}\!-\!\vdots\!-\!\text{CH}_2 \\
\overset{\bullet}{\text{CH·OMe}} \quad\quad \overset{\bullet}{\text{CH·OMe}} \\
\text{CH·OMe} \quad\quad \overset{\bullet}{\text{CH}} \\
\overset{\bullet}{\text{CH}} \quad\quad\quad \text{O}\left[\overset{\bullet}{\text{CH·OMe}}\right. \\
\overset{\bullet}{\text{CH·OMe}} \quad\quad \overset{\bullet}{\text{CH·OMe}} \\
\overset{\bullet}{\text{CH}_2\text{·OMe}} \quad\quad \text{CH·OMe}
\end{array}\right.
}}
\xrightarrow{+2\text{H}_2\text{O}}
\begin{array}{l}
\text{O}\left[\begin{array}{l} \text{CH·OH} \\ \overset{\bullet}{\text{CH·OMe}} \\ \text{CH·OMe} \\ \overset{\bullet}{\text{CH}} \end{array}\right. \\
\overset{\bullet}{\text{CH·OMe}} \\
\overset{\bullet}{\text{CH}_2\text{·OMe}}
\end{array}
+
\begin{array}{l}
\text{CH}_2\text{·OH} \\
\overset{\bullet}{\text{CH·OMe}} \\
\text{O}\left[\begin{array}{l} \overset{\bullet}{\text{CH}} \\ \overset{\bullet}{\text{CH·OMe}} \\ \overset{\bullet}{\text{CH·OMe}} \\ \overset{\bullet}{\text{CH·OH}} \end{array}\right.
\end{array}
$$

Heptamethyl methylmaltoside.   Tetramethyl glucose.   Trimethyl glucose.

(VII.)   (VIII.)   (II.)
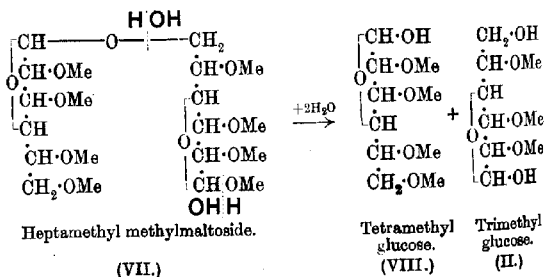
Inasmuch as ordinary crystalline maltose is hydrolysed by contact with the enzyme maltase and not by emulsin, the disaccharide is to be regarded as glucose-α-glucoside, and since it exhibits an

upward mutarotation and belongs to the d-series, it may be described stereochemically as β-glucose-α-glucoside, and is structurally represented by formula I (p. 809). isoMaltose has probably the same structure, but is a glucose-β-glucoside. Maltose resembles melibiose in its behaviour (Bau, *Chem. Zeit*, 1897, **21**, 186), and so also cellobiose has properties in common with lactose (Hudson, *loc. cit.*). Definite structural formulæ have been assigned to one member in each of these pairs of disaccharides, namely, lactose and maltose, and it is legitimate, therefore, to assign a provisional structural formula to cellobiose (IX), especially in view of the fact that Denham and Woodhouse isolated from methylated cellulose on hydrolysis the same crystalline trimethyl glucose as the present authors obtained from methylated lactose (T., 1917, 111, 244; 1918, **113**, 188). This cellobiose formula is of the same structural type as lactose:

$$
\begin{array}{l}
\quad\quad\quad\quad\quad\quad CH_2 \cdot OH \\
\lceil CH \text{———} O \text{——} \dot{C}H \\
\mid \dot{C}H \cdot OH \quad\quad\quad \lceil \dot{C}H \\
O \mid \dot{C}H \cdot OH \quad\quad\quad \mid \dot{C}H \cdot OH \\
\mid \dot{C}H \quad\quad\quad\quad\quad O \mid \dot{C}H \cdot OH \\
\llcorner \dot{C}H \quad\quad\quad\quad\quad \mid \dot{C}H \cdot OH \\
\quad \dot{C}H \cdot OH \quad\quad\quad \llcorner \dot{C}H \cdot OH \\
\quad \dot{C}H_2 \cdot OH
\end{array}
$$

Cellobiose.
(IX.)
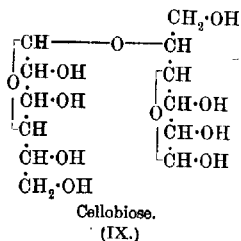
Experiments are at present in progress to confirm this provisional constitution.

EXPERIMENTAL.

Methylation of Maltose with Methyl Sulphate: Preparation of Heptamethyl Methylmaltoside.

Maltose (30 grams) prepared by the action of barley diastase on potato starch was dissolved in the minimum volume of warm water. To the cooled solution methyl sulphate (28·5 c.c.) was added, and a 30 per cent. solution of sodium hydroxide (29 c.c.) was introduced very gradually with stirring. During the addition of the latter, the temperature was maintained at 35—40°, and the mixture kept overnight. The reducing action of the maltose towards Fehling's solution had then completely disappeared, and methylmaltoside had obviously been formed. The methylation of the remaining hydroxyl groups was effected at 70°, and the solution maintained faintly alkaline throughout. Methyl sulphate (85·5 c.c.) was added slowly at this temperature with efficient

mechanical stirring, and simultaneously 30 per cent. sodium hydr-oxide (82 c.c.) was introduced. It is important that the reagents should be added very gradually; a separate dropping funnel was kept for each reagent. The second part of the methylation, which has just been described, occupied one and a-half hours, after which the temperature was raised to 100° for half an hour. Extraction of the methylated maltoside with chloroform yielded, after drying over anhydrous magnesium sulphate and distillation of the solvent, 39 grams of a crude, straw-yellow syrup. This was subjected to another similar methylation at 70° with methyl sulphate, and, after careful removal of the whole of the chloroform used for the extraction, the residue weighed 28·2 grams.

By distillation in the high vacuum of the Gaede pump, 23 grams of a colourless syrup were collected at about 195°/0·28 mm. In order to ensure complete methylation of all the hydroxyl groups, this product was again methylated with alternative reagents, namely, with silver oxide and methyl iodide. The material was isolated in the usual way after this treatment, and yielded a colour-less syrup distilling at 187°/0·06 mm. All the still residues were again methylated, and provided a further quantity of the required product. At this stage, the material from several preparations was combined and redistilled, when almost the whole distilled at 189—190°/0·09 mm., and showed n_D 1·4698. The compound was devoid of any reducing action on Fehling's solution, and behaved as a glucoside.

A methoxyl estimation indicated that complete methylation had taken place, eight methoxyl groups having been inserted in the maltose residue :

0·1290 gave 0·2493 CO_2 and 0·0957 H_2O. C = 52·7; H = 8·24.
0·0995 ,, 0·4034 AgI. OMe = 53·52.

$C_{12}H_{14}O_3(OMe)_8$ requires C = 52·86; H = 8·37; OMe = 54·63 per cent.

The specific rotation of the heptamethyl methylmaltoside was determined in various solvents as follows :

Solvent.	c.	a_D.
Methyl alcohol	1·313	+89·5°
Ethyl alcohol	1·395	+89·6°
Acetone	1·173	+89·5°
Water	1·345	+81·4°

As the specific rotation in water appears slightly lower than was expected, an opportunity will be taken to confirm this value.

Hydrolysis of Heptamethyl Methylmaltoside.

Preliminary experiments indicated that the hydrolysis could best be effected with 5 per cent. aqueous hydrochloric acid solution at 85—100°. These conditions were also observed with the main bulk of the material, weighing 30 grams, which was dissolved in 400 c.c. of dilute acid of the above concentration. The solution was heated for one and a-half hours at 85°, and for a similar period at 100°. The mixture showed an initial rotation of $\alpha + 12\cdot9°$, and the final reading was $9\cdot8°$. Further heating of a small sample of the solution produced no change in the rotation value. The procedure for the isolation of the products consisted in neutralisation with excess of barium carbonate, followed by filtration and evaporation of the filtrate under diminished pressure, when a syrup contaminated with barium chloride was obtained. The mineral matter was removed by extraction of the syrup with alcohol. After removal of this solvent, the residue was extracted with ether and the ethereal solution distilled. The syrup isolated in this way weighed 25 grams, and was carefully fractionated in a high vacuum.

Fraction   I.—B. p. 120—131°/0·3 mm. Weight, 8·2 grams.
     ,,   II.—B. p. 131—155°/0·23 mm. Weight, 8·4 grams.
     ,,   III.—B. p. 171°/0·23 mm. Weight, 5·4 grams.

The first of these fractions crystallised immediately on nucleation with a specimen of tetramethyl glucose of the butylene oxide form. Fraction II was obviously a transition fraction which partly crystallised, and from it further quantities of the first and third fractions were ultimately obtained by repeated distillation. Fraction III had a boiling point which corresponded with that of a trimethyl hexose. All the fractions were colourless syrups which failed to give osazones and were not easily oxidised with permanganate. A recrystallisation of fraction I produced the easily recognisable needles of tetramethyl glucose, and its identity with this compound was shown by the rotatory power (see Purdie and Irvine, T., 1904, **85**, 1049), which was $[\alpha]_D + 83°$ (equilibrium value) in water. Moreover, the melting point was correct for this substance, and a mixed melting-point determination showed no depression. The isolation of this substance from methylated maltose confirms the earlier observation recorded by Purdie and Irvine (T., 1905, **87**, 1029).

An analysis of fraction III, which showed n_D 1·4792, gave the following results:

0·1394 gave 0·2480 CO_2 and 0·1060 H_2O.　C=48·52; H=8·02.

$C_9H_{18}O_6$ requires C=48·62; H=8·11 per cent.

An estimation of the methoxyl content characterised the substance as a trimethyl hexose:

0·1120 gave 0·3527 AgI.　OMe=41·6.

$C_6H_9O_3(OMe)_3$ requires OMe=41·9 per cent.

The specific rotatory power of the trimethyl hexose was determined as follows:

Solvent.	c.	a_D.
Methyl alcohol	2·123	+67·8°
Acetone	2·151	+61·4°
Water	1·816	+69·3° —→ 71·0° (final value)

Oxidation.—With the object of determining the constitution of this hexose derivative, which clearly must represent one of the glucose residues of the maltose molecule, and therefore must be a trimethyl glucose, 3·5 grams of the substance were oxidised by gentle digestion with 40 c.c. of dilute nitric acid (D 1·2).　To initiate the reaction, the temperature was maintained at 80° for a few minutes, and thereafter at 68° for three and a-half hours. Nitrous fumes had ceased to be evolved by this time, and the solution was almost colourless.　The water was evaporated under diminished pressure at 35—40°; more water was repeatedly added during this procedure, and the solution again concentrated with the view of removing the whole of the nitric acid.　Similar treatments with ethyl alcohol, followed by evaporation in a vacuum, served to eliminate the mineral acid, and the procedure was repeated with dry ether.　Finally, a pale yellow syrup was obtained, which was dried and prepared for analysis by heating at 90° in a vacuum while passing through it a current of dry air. The weight of this oxidation product was 2·7 grams:

0·1094 gave 0·1847 CO_2 and 0·0618 H_2O.　C=46·03; H=6·26.

0·0999 　,,　 0·2720 AgI.　OMe=35·9.

$C_6H_5O_4(OMe)_3$ requires C=46·15; H=6·0; OMe=39·7 per cent.

From the above figures, the substance appeared to be a trimethyl saccharolactone, and this view was confirmed by titration with alkali.

0·0995 Gram was dissolved in dilute alcohol and rapidly titrated with $N/10$-sodium hydroxide, using phenolphthalein as indicator.　When about 4·5 c.c. of the standard alkali had been added, the colour of the indicator remained for a few minutes and then disappeared.　With each subsequent addition of alkali up to the amount of 9 c.c., the same phenomenon was observed. Excess of alkali was now introduced and the solution heated for

half an hour, and finally titrated to neutral point with standard acid. The amount of $N/10$-sodium hydroxide required for the complete neutralisation was 9·8 c.c., whereas a lactonic acid of the formula $C_9H_{14}O_7$ requires 9·7 c.c.

The specific rotation of trimethyl saccharolactone was determined in aqueous solution, and showed $[\alpha]_D 78°$, falling to the value $+40°$ after four hours. On catalysis with a trace of hydrochloric acid, the value again increased to $+56°$. A molecular weight determination in acetone solution by the ebullioscopic method gave the number 242, whilst the molecular weight required by the formula of the lactonic acid, $C_9H_{14}O_7$, is 234.

The authors are grateful to the Carnegie Trust for the grant of a Research Fellowship to one of them.

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LXIV.—*Condensation of Deoxybenzoin and Aldehydes.*

By ANANDA KISORE DAS and BROJENDRA NATH GHOSH.

IT has been shown that aromatic *o*-hydroxy-aldehydes condense with substances containing ·CO·CH$_2$·CO· groups as in 1:3-diketo-hydrindene (Sastry and Ghosh, T., 1915, **107**, 1442), and in acetyl or benzoyl acetone (Chatterjee and Ghosh, T., 1918, **113**, 444) to form pyranol derivatives of the type
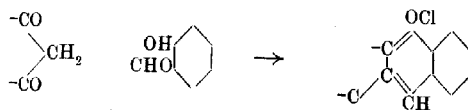
In order to extend this investigation, a substance of a similar type, namely, deoxybenzoin, was employed. In this case, instead of a ·CO·CH$_2$·CO· group, a ·CH$_2$· group is situated between one ·CO· group and the other phenyl group.

Several investigators have studied the interaction of benzaldehyde and deoxybenzoin, both acid and alkali being used as condensing agents (Japp and Klingemann, *Ber.*, 1888, **21**, 2935; Knoevenagel and Weissgerber, *Ber.*, 1893, **26**, 337; Stobbe and Niedenzu, *Ber.*, 1901, **34**, 3897; Klages and Tetzner, *Ber.*, 1902, **35**, 3971).

As our object was to synthesise pyranol derivatives, we began

H H*

with the condensation of salicylaldehyde and deoxybenzoin. It appeared that in the presence of alkali hydroxides, the condensation might proceed in the following way:

$$\begin{matrix} \text{COPh} \\ \text{CH}_2\text{Ph} \end{matrix} + \begin{matrix} \text{OH} \\ \text{CHO} \end{matrix} \bigcirc \rightarrow \begin{matrix} \text{COPh OH} \\ \text{CPh}{=}\text{CH} \end{matrix} \bigcirc ,$$
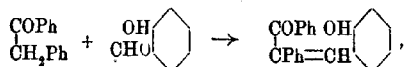
giving salicylidenedeoxybenzoin, which in the presence of hydrogen chloride might yield 2:3-diphenylbenzopyronium chloride (I).

$$\begin{matrix} & \text{OCl} \\ \text{PhC} & \diagup \\ \text{PhC} & \\ & \text{CH} \end{matrix}$$

(I.)
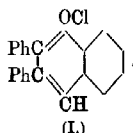
Accordingly, we conducted the reaction in the presence of alkali hydroxide, but found that no condensation took place under the conditions of the experiment. With hydrogen chloride, however, we obtained the desired compound. Decker and von Fellenberg (*Annalen,* 1909, **364**, 31) obtained the corresponding ferrichloride.

It was also found that no interaction took place between *p*-hydroxybenzaldehyde and deoxybenzoin in the presence of alkali hydroxide, but with hydrogen chloride the condensation product was formed; it could not, however, be obtained in a pure state.

Failing to obtain condensation products in the above two cases with alkali hydroxide, we extended the experiment to other aldehydes, such as anisaldehyde, piperonal, and *p*-tolualdehyde, using both alkali hydroxide and hydrogen chloride as condensing agents. In each case, a distinct condensation product was isolated. At present we are not in a position to offer an explanation of the apparent inactivity of *o*- and *p*-hydroxybenzaldehyde and deoxybenzoin in the presence of alkali hydroxide, but hope to deal with this point in a future communication.

EXPERIMENTAL.

Attempted Condensation of Salicylaldehyde and Deoxybenzoin in the Presence of Alkali Hydroxide.

1·2 Grams of salicylaldehyde and deoxybenzoin were dissolved in methyl alcohol, and to the mixture 3 grams of potassium hydroxide dissolved in 5 c.c. of water were added. The whole was then heated for two hours. A clear solution was obtained which, on the addition of water, gave a crystalline substance. This was collected, and the solution was acidified, but no solid substance separated.

2 : 3-*Diphenylbenzopyronium Chloride* (I).

A solution of 2 grams of deoxybenzoin and 1·2 grams of salicyl-aldehyde in methyl alcohol was saturated with dry hydrogen chloride. The colour of the solution changed from yellow to pink. It was kept overnight, but no precipitate separated. On the addition of very dilute hydrochloric acid, a dark red substance separated, which was dissolved in alcohol and reprecipitated by the addition of dilute hydrochloric acid, collected, washed with dilute hydrochloric acid, and kept in a vacuum over potassium hydroxide. On long keeping, it gradually became viscid. A portion of it, which was crystalline, was analysed:

0·1668 gave 0·4827 CO_2 and 0·0750 H_2O. $C = 78·9$; $H = 5·0$.

$C_{21}H_{15}OCl$ requires $C = 79·1$; $H = 4·7$ per cent.

The compound darkens at 85° and melts and decomposes at 176°.

Attempted Condensation of p-*Hydroxybenzaldehyde and Deoxybenzoin in the Presence of Alkali Hydroxide.*

A methyl-alcoholic solution of 1·2 grams of *p*-hydroxybenz-aldehyde and 2 grams of deoxybenzoin was heated for about an hour with 3 grams of potassium hydroxide dissolved in 5 c.c. of water. A clear liquid was obtained, which was acidified as before, but nothing separated.

A condensation product was, however, obtained with hydrogen chloride as the condensing agent, but this compound could not be crystallised, and as it melted very indefinitely (170—185°), it appeared to be a mixture which could not be easily separated.

α-p-*Methoxybenzylidenedeoxybenzoin.*

A current of dry hydrogen chloride was passed through a methyl-alcoholic solution of molecular quantities of anisaldehyde and deoxybenzoin for a few minutes. After allowing the solution to remain for two days, a crystalline substance separated, which was collected and recrystallised from alcohol. It separated in colour-less needles melting at 113°. (Found: $C = 83·77$; $H = 5·8$. $C_{22}H_{18}O_2$ requires $C = 84·09$; $H = 5·70$ per cent.)

p-*Methoxy-α-chlorobenzyldeoxybenzoin.*

This was prepared by supersaturating a methyl-alcoholic solu-tion of molecular quantities of anisaldehyde and deoxybenzoin with

H H 2*

dry hydrogen chloride. The substance began to separate at once from the solution, and was collected next day. It was recrystal-lised from acetic acid, when it separated in colourless needles melt-ing and decomposing at 152° (Klages and Tetzner give 144°). On testing the substance, it was found to contain chlorine. (Found: $C = 75.50$; $H = 5.60$. $C_{22}H_{19}O_2Cl$ requires $C = 75.40$; $H = 5.40$ per cent.)

It may be noted here that 3:4-methylenedioxy-α-chlorobenzylde-oxybenzoin and p-methyl-α-chlorobenzyldeoxybenzoin were similarly obtained.

3 : 4-*Methylenedioxybenzamarone*,

$$CH_2\!\!<^O_O\!\!>C_6H_3 \cdot CH(CHPh \cdot COPh)_2.$$
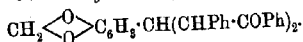
This was prepared by heating a methyl-alcoholic solution of 4 grams of deoxybenzoin and 1·5 grams of piperonal with 3 grams of potassium hydroxide dissolved in 5 c.c. of water. The sub-stance which separated was collected, washed, and crystallised from acetic acid, when colourless needles melting at 243—244° were obtained:

0·1347 gave 0·4031 CO_2 and 0·0673 H_2O. $C = 82.38$; $H = 5.50$.
$C_{36}H_{28}O_4$ requires $C = 82.40$; $H = 5.30$ per cent.

p-*Methylbenzamarone*, $C_6H_4Me \cdot CH(CHPh \cdot COPh)_2.$

This was prepared by boiling a methyl-alcoholic solution of 1·2 grams of p-tolualdehyde and 4 grams of deoxybenzoin with 3 grams of potassium hydroxide in 5 c.c. of water. The substance crystallised from acetic acid in colourless needles melting at 233—234°:

0·1103 gave 0·3461 CO_2 and 0·0676 H_2O. $C = 85.50$; $H = 6.80$.
$C_{36}H_{30}O_2,\tfrac{1}{2}H_2O$ requires $C = 85.80$; $H = 6.30$ per cent.

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LXV.—*Condensation of Deoxybenzoin with Aromatic Aldehydes.*

By BAWA KARTAR SINGH and JATINDRA KUMAR MAZUMDAR.

HIS work was undertaken with the object of extending the nalogy which exists between deoxybenzoin and 1:3-diketones, 1asmuch as both these substances may be condensed with aryl ldehydes by Knoevenagel's reaction. In the case of deoxybenzoin, t is the negative phenyl group that influences the reactivity of he hydrogen atoms of the methylene group, and thus acts similarly o one of the carbonyl groups in the 1:3-diketones:

$$CO \cdot CH_2 \cdot CO \cdot \ + \ R \cdot CHO \ \longrightarrow \ \begin{matrix} CO \cdot C \cdot CO \cdot \\ \| \\ R \cdot CH \end{matrix}$$

$$C_6H_5 \cdot CH_2 \cdot CO \cdot C_6H_5 + R \cdot CHO \ \longrightarrow \ \begin{matrix} C_6H_5 \cdot C \cdot CO \cdot C_6H_5 \\ \| \\ R \cdot CH \end{matrix}$$
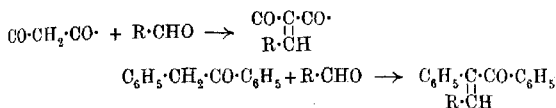
With this object in view, several aryl aldehydes, namely, salicyl-aldehyde, *p*-hydroxybenzaldehyde, 2-naphthol-1-aldehyde, cinnam-aldehyde, vanillin, *o*-aminobenzaldehyde, *p*-dimethylaminobenz-aldehyde, piperonal, and *o*- and *p*-nitrobenzaldehyde* were con-densed with deoxybenzoin through the agency of hydrogen chloride, alcoholic potassium hydroxide, and diethylamine.
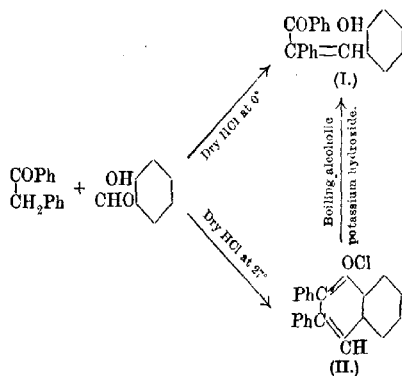
* It was subsequently found that deoxybenzoin had already been ondensed with piperonal, and *o*- and *p*-nitrobenzaldehyde by Stobbe and Wilson (*Annalen*, 1910, 374, 237) ; these compounds are therefore omitted rom this paper.

In the course of this work, it has been observed that different results are obtained by condensing deoxybenzoin and salicyl-aldehyde with hydrogen chloride at 0° and at 27°. At 0°, salicyl-idenedeoxybenzoin (I) is obtained, whilst at 27° pyranol formation takes place, as previously observed by Decker and von Fellenberg (*Annalen*, 1909, **364**, 1). These authors isolated the product in the form of the ferrichloride, but we isolated the hydrochloride (II) direct.

<center>EXPERIMENTAL.</center>

<center>*Salicylidenedeoxybenzoin* (I).</center>

0·8 Gram of salicylaldehyde was mixed with an alcoholic solu-tion of 1 gram of deoxybenzoin. The mixture was cooled in ice and saturated with dry hydrogen chloride, when the colour of the solution changed to dark brown. The mixture was kept for two to three days, when an amorphous, brown precipitate formed, which was collected and crystallised twice from dilute alcohol. The substance darkens at 120° and melts at 160°. It is soluble in alcohol or acetic acid, but insoluble in water:

0·1850 gave 0·5686 CO_2 and 0·1042 H_2O. C = 83·6; H = 6·0.

$C_{21}H_{16}O_2$ requires C = 84·0; H = 5·40 per cent.

0·2 Gram of the substance was boiled under reflux with 10 c.c. of 50 per cent. alcoholic potassium hydroxide for two hours. The substance dissolved with change of colour. On cooling and acidifying with dilute hydrochloric acid, the original substance was precipitated.

Condensation of salicylaldehyde with deoxybenzoin could not be effected through the agency of potassium hydroxide, although various methods were tried.

<center>2:3-*Diphenylbenzopyronium Chloride* (II).</center>

1·5 Grams of salicylaldehyde were mixed with 2 grams of deoxy-benzoin dissolved in a small quantity of methyl alcohol. Dry hydrogen chloride was then passed through the mixture for two hours at 27°; a very bright deep red coloration was developed, and the solution acquired a syrupy consistency. On keeping for two days, red, needle-shaped crystals separated. They were collected and recrystallised from dilute acetic acid containing a little hydro-chloric acid, when they formed red needles melting at 100°. The substance is soluble in alcohol or acetic acid, but insoluble in water:

0·1550 gave 0·4582 CO_2 and 0·0700 H_2O.   C = 80·6; H = 5·0.

$C_{21}H_{15}OCl$ requires C = 79·1; H = 4·7 per cent.

0·5 Gram of the above pyranol compound was dissolved in alcohol and boiled under reflux with 20 c.c. of 10 per cent. alcoholic potassium hydroxide for three hours.   The solution was then diluted with water and acidified with dilute acetic acid.   The brown precipitate was collected, dissolved in alcohol, and again precipitated by water.   It was identified as the compound (I), darkening. at 120° and melting at 160°.   (Found: C = 83·5; H = 6·0. $C_{21}H_{16}O_2$ requires C = 84·0; H = 5·4 per cent.)

2 : 3-*Diphenylnaphthapyronium Chloride*,
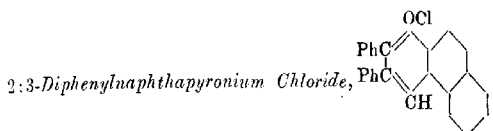
Two grams of deoxybenzoin and 1·6 grams of 2-naphthol-1-aldehyde were dissolved in methyl alcohol, and dry hydrogen chloride was passed into the solution for three hours at the ordinary temperature (25°).   The solution gradually acquired a dark blue colour, and, after two to three days, dark blue needles separated. They were collected, washed with a little methyl alcohol, and re-crystallised from dilute acetic acid, when they melted at 148—150°.

The compound is soluble in acetic acid, alcohol, or ether, but insoluble in water:

0·1255 gave 0·3738 CO_2 and 0·0566 H_2O.   C = 81·16; H = 5·01.

$C_{25}H_{17}OCl$ requires C = 81·41; H = 4·61 per cent.

This substance decomposes gradually on keeping.   It has been isolated in the form of the ferrichloride by Decker and von Fellenberg (*loc. cit.*).

4-*Hydroxy*-2 : 3-*diphenylquinoline*,
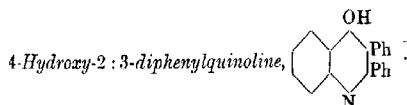
Two grams of deoxybenzoin and 1·6 grams of anthranilic acid were mixed together, powdered, and heated in an oil-bath at 30—150° for three days.   The product was then rendered alkaline with dilute sodium hydroxide solution and extracted with ether.   The aqueous portion was acidified with dilute acetic acid and again extracted with ether.   A solid gradually separated from

the aqueous solution. This was collected, washed, and crystallised from alcohol, when colourless, rectangular cubes melting at above 300° were obtained. The compound is insoluble in water, soluble in acetic acid or ether, and sparingly so in aqueous sodium hydroxide or alcohol:

0·1357 gave 5·8 c.c. N_2 at 32° and 762 mm. $N = 4·8$.

$C_{21}H_{15}ON$ requires $N = 4·53$ per cent.

p-*Hydroxybenzylidenedeoxybenzoin,* $\begin{array}{l} COPh \\ CPh{:}CH \end{array}$ ⟨⟩OH
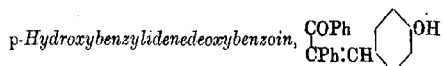
p-Hydroxybenzaldehyde and deoxybenzoin in molecular proportion were dissolved in a small quantity of ethyl alcohol, and the solution was cooled in ice and saturated with dry hydrogen chloride, when a change of colour took place at once. On allowing the mixture to remain for two to three days, a precipitate gradually formed, which was collected and crystallised from dilute acetic acid, separating in red needles melting at 155°. The substance is soluble in alcohol or acetic acid, but insoluble in water. It does not contain chlorine:

0·1460 gave 0·4465 CO_2 and 0·0722 H_2O. $C = 83·4$; $H = 5·5$.

$C_{21}H_{16}O_2$ requires $C = 84·0$; $H = 5·4$ per cent.

Vanillylidenedeoxybenzoin, $\begin{array}{l} COPh \\ CPh{:}CH \end{array}$ ⟨⟩$\begin{array}{l} OH \\ OMe \end{array}$.
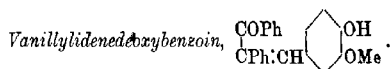
Vanillin and deoxybenzoin in molecular proportion were condensed as above, when an oil was obtained which solidified in three to four days. This separated from hot alcohol as an amorphous, reddish mass melting at 146—148°. It is soluble in acetic acid, alcohol, or ether, but insoluble in water. It does not contain chlorine:

0·1274 gave 0·3755 CO_2 and 0·0596 H_2O. $C = 80·4$; $H = 5·3$.

$C_{22}H_{18}O_3$ requires $C = 80·0$; $H = 5·4$ per cent.

Cinnamylidenedeoxybenzoin hydrochloride,

$\begin{array}{l} COPh \\ CHPh{\cdot}CHCl{\cdot}CH{:}CH \end{array}$ ⟨⟩
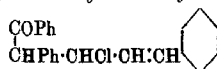
Deoxybenzoin and cinnamaldehyde in molecular proportion were condensed as above, and there was obtained a solid which separated from hot alcohol as an amorphous mass melting at 100°.

It is soluble in alcohol, acetic acid, or ether, but insoluble in water. The substance contains chlorine:

0.1238 gave 0.3609 CO_2 and 0.0657 H_2O.   C=79.5; H=5.9.

$C_{23}H_{19}OCl$ requires C=79.7; H=5.5 per cent.

Cinnamylidenedeoxybenzoin, $\begin{matrix}COPh \\ CPh\text{:}CH\cdot CH\text{:}CH\end{matrix}$ ⬡ .
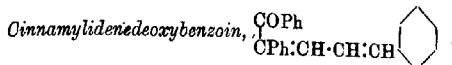
Deoxybenzoin and cinnamaldehyde in molecular proportion were dissolved in a little alcohol, and the mixture was cooled in ice, a few drops of diethylamine being added. A crystalline precipitate formed within an hour, which separated from hot glacial acetic acid in snow-white needles melting at 145°. The yield was almost theoretical.

It is insoluble in water and sparingly soluble in ethyl alcohol or acetic acid:

0.1095 gave 0.3558 CO_2 and 0.0601 H_2O.   C=88.6; H=6.1.

$C_{23}H_{18}O$ requires C=89.0; H=5.8 per cent.

p-Dimethylaminobenzylidenedeoxybenzoin, $\begin{matrix}COPh \\ CPh\text{:}CH\end{matrix}$ ⬡ NMe_2 .
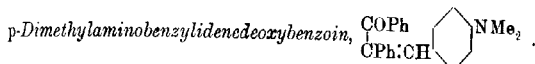
p-Dimethylaminobenzaldehyde and deoxybenzoin in molecular proportion were condensed in the usual manner, and a solid was obtained which crystallised from dilute acetic acid in colourless needles melting at 98°. It is very readily soluble in ethyl alcohol or acetic acid, but insoluble in water:

0.1159 gave 4.6 c.c. N_2 at 28° and 761 mm.   N=4.6.

$C_{23}H_{21}ON$ requires N=4.3 per cent.

This work was carried out at Dacca College in 1917.

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    GOVERNMENT COLLEGE,
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LXVI.—*Trustworthiness of the Balance over Long Periods of Time.*

By GEORGE DEAN.

DURING the prosecution of a series of atomic-weight determinations by the author, a paper was published on "The limitations of the balance" (Blount, T., 1917, **111**, 1035). The author there draws the conclusion, based on experiments with several balances, that although weighings of a given object made within a few hours —or even days—of each other may be concordant, this is not the case if they are extended over several months. A variation as high as 1·6 milligrams was detected, and attributed to the gradual shifting of the central knife edge.

If this conclusion is established, the accuracy of many atomic-weight determinations will be seriously impaired. The work referred to above is especially liable to this error, as a period of three to fifteen months intervened between the initial and final weighings. Fortunately, it was possible to test the magnitude of the error in this case. The experiments were carried out in weighed silica flasks, each provided with a similar silica flask as counterpoise. These were used in successive experiments, and, being appreciably affected by the chemical action, their weights, recorded during several years, were useless for the present purpose. One flask, however, being of inconvenient shape, had been used, re-weighed, and rejected. It was weighed after long intervals. The details of the weighings are as follows, the numbers representing the weights added to the counterpoise to make it balance the flask.

May 17th, 1917. Flask treated with boiling
nitric acid, washed with
distilled water, dried,
wiped, ignited, cooled in
desiccator with counter,
and both left on pans of
balance before weighing $+0\cdot001300$ gram
May 18th, 1917. Merely replaced in balance
and left all night before
weighing . . . . $+0\cdot001325$,, $\Bigg\}$ $0\cdot001312$ gram.

The two were now left over calcium chloride under a bell glass for ten months.

Mar. 7th, 1918. Replaced in balance, left
all night and re-weighed $+0\cdot001360$ gram
Mar. 8th, 1918. Flask and counter, both
carefully wiped and re-
placed, left all night on
pans before weighing . $+0\cdot001379$,, $\Bigg\}$ $0\cdot001374$ gram.
Mar. 9th, 1918. Merely replaced and left
all night . . . . $+0\cdot001382$,,

After a further interval of two months, a single weighing was taken:

July 23rd, 1918. Flask, etc., replaced in balance and left all
                 night   .   .   .   . 0·001415 gram.

The flasks were now left in the desiccator for ten months, the balance remaining practically unused:

May 20th, 1919. Replaced in balance and
                 left all night .   .   . +0·001422 gram
  ,, 23rd ,,   Flask wiped and heated
                 (but not counter), cooled
                 in desiccator, in balance
                 all night .   .   .   . +0·001419 ,,
  ,, 26th ,,   Both replaced in balance
                 and left for week-end . +0·001406 ,,
  ,, 27th ,,   Counterpoise, wiped, ig.
                 nited,cooled in desiccator,   ' 0·001435 gram.
                 both left in balance all
                 night .   .   .   . +0·001474 ,,
  ,, 28th ,,   Both replaced in balance
                 and left all night ,.   . +0·001480 ,,
  ,, 31st ,,   Both in desiccator 2 days,
                 in balance 1 night .   . +0·001421 ,,
  June 3rd ,,   Both in desiccator 2 days,
                 in balance 1 night .   . +0·001425 ,,

The total variation in weight of a flask weighing 40·65 grams, in two years, is thus +0·000123 gram, made up of +0·000062 gram in the first ten months, +0·000041 gram in the succeeding four months, and 0·000020 gram in the final ten months.

After carrying out determinations extending over several years, and depending on some thousands of elaborate weighings, it was satisfactory to find the error introduced by the duration of an experiment was so small as to be practically negligible. The fact that the variation was a steady increase rather favours the view that it is due to a displacement of the knife edge.

The test was more searching than if twin metal weights had been used; the flasks were more bulky; they were polished occasionally by breathing upon them and rubbing with a cloth, this being necessary in the atomic-weight experiments to remove a slight film deposited on the flask from the oven in which it was heated. As each flask had an external surface of about 250 sq. cm., there is a possibility of changes in weight from this treatment, as also from air condensation after heating.

The weighings were not made under ideal conditions. The room is small and has a low ceiling, with two doors and windows, is heated by a steam radiator, and subject to vibration from a ventilating fan. To minimise these drawbacks, the flasks were placed on the balance the night before the weighing, the windows

heavily curtained, and fan and radiator turned off. In this way, trustworthy readings were secured.

The method of swings was used, ten swings of the pointer to the left and nine to the right being recorded, and the point of equilibrium on the scale calculated. The rider was next shifted along the beam to increase the weight by 1 milligram, and the observations were repeated. Finally, the flasks and rider were removed from the balance, which was then left for at least an hour. It was then set swinging, and the true "zero" of the empty balance worked out. From the three equilibrium positions, the weight of the flask is easily calculated. It was necessary to adopt this tedious method, as the "zero" of the balance is rarely constant for more than a few hours at a time.

The balance was an ordinary short-beam instrument of (unknown) German make. It was in constant use except during the final ten months, when no weighings were made on it except those recorded above.

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LXVII.—*The Isomeric Tropic Acids.*

By ALEX. MCKENZIE and JOHN KERFOOT WOOD.

ALTHOUGH nearly forty years have elapsed since Ladenburg carried out his fundamental researches on the constitution of atropine, this alkaloid is still obtained exclusively from natural sources. This is undoubtedly due to the difficulties involved in the preparation in quantity of the two constituents of the atropine molecule, namely, tropine and r-tropic acid. The yield of atropine obtained by Ladenburg by the combination of the two constituents according to the equation

$$CH_2 \cdot CH \!-\! CH_2 \qquad \qquad Ph$$
$$| \quad NMe \; CH \cdot OH \; + \; CO_2H \cdot CH$$
$$CH_2 \cdot CH \!-\! CH_2 \qquad \qquad CH_2 \cdot OH$$

$$CH_2 \cdot CH \!-\! CH_2 \qquad Ph$$
$$| \quad NMe \; CH \cdot O \cdot CO \cdot CH \qquad + H_2O$$
$$CH_2 \cdot CH \!-\! CH_2 \qquad CH_2 \cdot OH$$
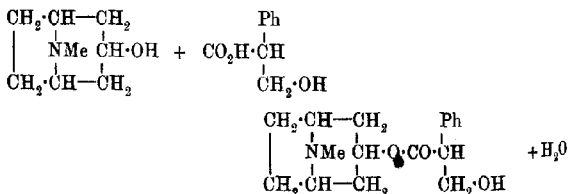
was apparently very small. Wolffenstein and Mamlock (*Ber.*, 1908, **41**, 723) have, however, shown that by acetylating tropic

acid, then converting into the acid chloride, and combining this with tropine, a good yield of acetylatropine hydrochloride can be obtained, and from the latter compound the acetyl group can be eliminated with the formation of atropine in a satisfactory yield. In the light of the experience of these authors, there should be no difficulty in effecting the synthesis of atropine in fair quantity provided that methods are available for the production of the requisite tropine and tropic acid.

The recent synthesis of tropinone by Robinson (T., 1917, **111**, 762) suggests the possibility of the production of synthetic tropine. Meanwhile, the present authors had been engaged in the examination of various methods for the preparation of tropic acid other than that from atropine itself, and the results are described in the present communication.

Ladenburg and Rügheimer (*Ber.*, 1880, **13**, 373; *Annalen*, 1883, **217**, 74) claim to have converted atropic acid into tropic acid in the following manner. Chlorotropic acid was first obtained by the direct addition of hypochlorous acid to atropic acid,

$$CH_2:CPh \cdot CO_2H + HClO = OH \cdot CH_2 \cdot CClPh \cdot CO_2H,$$
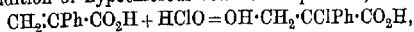
and the chlorotropic acid was then reduced,

$$OH \cdot CH_2 \cdot CClPh \cdot CO_2H + 2H = OH \cdot CH_2 \cdot CHPh \cdot CO_2H + HCl.$$
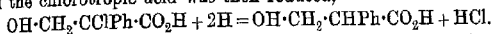
It is apparent from Ladenburg's description that some difficulty was experienced by him in the reduction of the chlorotropic acid, although it is stated that the action proceeded smoothly when a mixture of zinc dust and iron filings was added to a solution of the acid in concentrated potassium hydroxide. It may be stated at once that our experience with this method was most disappointing. There was no difficulty in preparing the chloro-acid, but all our attempts to reduce it to tropic acid, whether by Ladenburg's method or in other ways, ended in failure. In many of these experiments the chloro-acid was partly recovered, whilst in one or two cases the product was free from halogen and possessed the melting point of atroglyceric acid. In view of the difficulties encountered, we drew the conclusion that this method is not a practical one for the preparation of appreciable quantities of tropic acid.

Spiegel (*Ber.*, 1881, **14**, 235) obtained tropic acid by heating acetophenonecyanohydrin with hydrochloric acid at 130°, and then acting on the resulting β-chlorohydratropic acid with a solution of sodium carbonate at 120°. There are no details quoted in the paper regarding the yield of tropic acid.

A method which we employed was the reduction of the formyl-phenylacetic ester, prepared by Wislicenus's method, from ethyl formate and ethyl phenylacetate. This ester was reduced in

ethereal solution by means of aluminium amalgam, and the result ing tropic ester was hydrolysed:

$$\text{CH}_2\text{Ph·CO}_2\text{Et} \longrightarrow \text{CHO·CHPh·CO}_2\text{Et} \longrightarrow$$
$$\text{OH·CH}_2\text{·CHPh·CO}_2\text{Et} \longrightarrow \text{OH·CH}_2\text{·CHPh·CO}_2\text{H.}$$
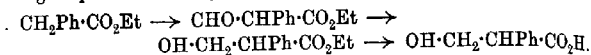
After these experiments were completed by us, the method was described by Müller (*Ber.*, 1918, **51**, 252; D.R.-P. 302737), and also by Wislicenus and Bilhuber (*Ber.*, 1918, **51**, 1237), the latter chemists having used methyl formylphenylacetate. Müller states that the aluminium residue retains almost half of the formyl ester, which is therefore not reduced, and, according to him, cannot be removed from the residue by means of ether. Wislicenus and Bilhuber also noticed that a portion of the formyl ester was retained by the aluminium. We also obtained a small yield of tropic acid by this process.

Of the methods we have studied for the preparation of tropic acid, the following gave by far the best result. Acetophenone was converted into atrolactinic acid, which, on being heated under diminished pressure, gave atropic acid; this in turn was converted into β-chlorohydratropic acid by the action of hydrogen chloride on its ethereal solution, and the halogen was then displaced by boiling the acid with an aqueous solution of sodium carbonate:

$$\underset{\text{Me}}{\overset{\text{Ph}}{>}}\text{CO} \longrightarrow \underset{\text{Me}}{\overset{\text{Ph}}{>}}\text{C}\underset{\text{CN}}{\overset{\text{OH}}{<}} \longrightarrow \underset{\text{Me}}{\overset{\text{Ph}}{>}}\text{C}\underset{\text{CO}_2\text{H}}{\overset{\text{OH}}{<}} \longrightarrow$$

$$\underset{\text{H}_2\text{C}}{\overset{\text{Ph}}{>}}\text{C·CO}_2\text{H} \longrightarrow \underset{\text{ClH}_2\text{C}}{\overset{\text{Ph}}{>}}\text{C}\underset{\text{CO}_2\text{H}}{\overset{\text{H}}{<}} \longrightarrow \underset{\text{OH·CH}_2}{\overset{\text{Ph}}{>}}\text{C}\underset{\text{CO}_2\text{H}}{\overset{\text{H}}{<}}$$
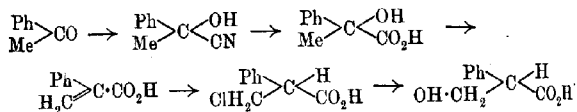
The resolution of *r*-tropic acid into its optically active components is described by Ladenburg and Hundt (*Ber.*, 1889, **22**, 2591). The acid was dissolved in dilute aqueous alcohol and neutralised by quinine. The resulting salt was crystallised until the melting point was constant, the value 186—187° being given. The tropic acid obtained from this salt melted at 127—128°, and gave [α]_D +71·4° "als Mittel aus Versuchen in verschieden concentrirten Lösungen." This value for the specific rotatory power of the *d*-acid has no significance, since the solvent employed is not quoted.

Amenomiya (*Arch. Pharm.*, 1902, **240**, 498) acted on a mixture of 10 grams of atropine and *l*-hyoscyamine with water, and obtained a mixture of *r*-tropic acid and a small quantity of the *l*-isomeride. This was neutralised with quinine, and the resolution conducted according to Ladenburg and Hundt. The quinine *d*-salt melted at 189—190°. The resulting acid was washed with benzene to free it from atropic acid; it then melted at 126—127°, whilst the value

$[a]_D^{20} + 71\cdot3°$ for $c = 2\cdot384$ in ethyl-alcoholic solution is quoted. From the mother liquors of the quinine salt, a lævorotatory tropic acid melting at 126° and giving $[a]_D^{20} - 72\cdot75°$ in aqueous solution was prepared. No analyses of the optically active acids are quoted either by Ladenburg and Hundt or by Amenomiya. Moreover, the quantity of inactive acid at the disposal of those investigators would seem to have been rather inadequate for the purpose they had in view.

Atropine is the *dl*-tropyl ester of tropine, whilst *l*-hyoscyamine is the *l*-tropyl ester of tropine. Hyoscyamine has the grouping ·CO·CH·, and, in accordance with the work carried out by one of us and his co-workers on racemisation with alcoholic alkali, it might be expected that this alkaloid would undergo racemisation with alcoholic alkali. Data in the literature show that this is the case, but the point is perhaps worthy of further investigation. Pure atropine is optically inactive, but the atropine of commerce is often slightly lævorotatory, owing to its containing some hyoscyamine. In all probability, the plant builds up the pure *l*-hyoscyamine, and this is racemised either in the plant itself or during the commercial preparation of atropine. The question (which probably has received attention from the manufacturers of atropine) suggests itself: Would it be possible to isolate pure hyoscyamine from the plant, or would this compound racemise so readily that its isolation on the large scale would be impossible? One of the sources of atropine is *Hyoscyamus muticus*—which is said to contain hyoscyamine only. Now it is significant that alkali always appears to be used in the extraction of atropine from plants. It might be possible technically to avoid the use of alkali in the extraction, and thus obtain a salt of pure hyoscyamine. If this were practical, the advantage would be very great, since *l*-hyoscyamine in its mydriatic power is reported as being one hundred times as active as its *d*-isomeride. It would therefore be a much better mydriatic than atropine. Similar considerations apply to pilocarpine. It has, however, to be recognised that it is doubtful if the naturally occurring *l*-hyoscyamine or its *d*-isomeride has ever been prepared in a state of purity, and it seems very probable that Barrowcliff and Tutin (T., 1909, **95**, 1966) are correct when they suggest that the interesting physiological results of Cushny on the comparison of the *d*- and *l*-hyoscyamines were obtained with alkaloids which were not optically pure.

By the hydrolysis of *l*-hyoscyamine, Gadamer (*Arch. Pharm.*, 1901, **239**, 294) obtained a lævorotatory tropic acid melting at 123°—124° and having $[a]_D^{20} - 69\cdot49°$ in aqueous solution. A purer specimen was obtained by heating an aqueous solution of *l*-hyoscine;

the resulting acid was washed with benzene to free it from the small amount of atropic acid present, and the residue then crystallised from water. The resulting tropic acid melted at 125—126° and gave $[\alpha]_D$ −71·81° in aqueous solution.

As it appeared to the present authors to be of some importance to establish the purity of the d- and l-tropic acids, the resolution of the r-acid was carried out as described in the experimental portion of this paper. The d-acid was obtained by means of quinine, the solvent used being ethyl alcohol. It melted at 128—129° and had $[\alpha]_D^{15}$ +72·2° for $c=2·695$ in ethyl-alcoholic solution, a result which is nearly identical with that of Amenomiya, who found $[\alpha]_D$ +71·3°. We obtained the l-acid by means of morphine, the solvent being ethyl alcohol. This acid melted at 128—129°, and had $[\alpha]_D^{13}$ −72·5° for $c=2·578$ in ethyl-alcoholic solution and $[\alpha]_D^{15}$ −79·0° for $c=1·538$ in aqueous solution. The lævorotatory acid of Amenomiya, which gave $[\alpha]_D$ −72·75° in aqueous solution, and Gadamer's acid, with $[\alpha]_D$ −69·49° in aqueous solution, were therefore not optically pure.

The results described in the present paper were practically completed towards the end of 1917, but publication has been delayed owing to the pressure of other work. Since the present paper was written, King (this vol., p. 476) has described the resolution of tropic acid, and our values for the specific rotatory powers of the optically active acids are in close agreement with those given by him. It is therefore satisfactory that the constants for these important acids have at last been definitely settled.

EXPERIMENTAL.

Reduction of Ethyl Formylphenylacetate.

As the reduction of this ester has already been described in the literature, it is unnecessary to describe our experience of the method. The ester used was the liquid modification, which was prepared by the action of sodium on a mixture of ethyl phenyl-acetate and ethyl formate, and purified through the copper derivative, as described by Wislicenus. In the bulk of the experiments, the reducing agent employed was aluminium amalgam. The ester was also reduced by the action of sodium on a solution of the ester in glacial acetic acid. The yields of the pure recrystallised tropic acid varied from 16 to 30 per cent. of the theoretical, calculating from the phenylformylacetic ester used.

Preparation of Atrolactinic Acid.

This acid was prepared as described by McKenzie and Clough (T., 1912, **101**, 393). The following details of a typical preparation may be given.

To a mixture of 80 grams of potassium cyanide (98 per cent.), 100 grams of acetophenone, and 5 c.c. of water, fuming hydrochloric acid (D 1·2) was added from a dropping funnel at the rate of twelve to fifteen drops at a time, the mixture being shaken vigorously after each addition. This operation lasted for five hours, 15 c.c. of acid being added in each of the first two hours and 20 c.c. in each of the subsequent hours. During the first three hours, the mixture was maintained at the ordinary temperature, so that the acetophenone did not solidify, but towards the close it was cooled in ice-cold water. When the addition of the acid was complete, the mixture was allowed to remain for half an hour, and the oil then poured off and washed with water. A further small quantity of oil was obtained by adding water to the sludge left in the reaction flask. The oil was then poured into 200 c.c. of hydrochloric acid (D 1·2) and left overnight. Sodium hydroxide solution was added until the solution was neutral, and then three times the theoretical amount of the same alkali (calculated on the acetophenone used) was added, and the mixture distilled in a current of steam until the evolution of ammonia ceased. About 65 grams of acetophenone were recovered. The contents of the distillation flask were evaporated until the separation of solid started. On cooling, the crystals were separated and acidified with hydrochloric acid, using Congo-red as indicator. The atrolactinic acid was filtered off, the filtrate evaporated further, and cooled; the resulting crystals contained some sodium chloride, from which the acid was separated by means of ether. Some additional acid was obtained from the filtrates. The ethereal solution of the acid was dried with anhydrous magnesium sulphate, the ether expelled, and the atrolactinic acid crystallised from water. The yield was 35 grams of crystallised acid, and this corresponds with a yield of 73 per cent. on the acetophenone converted.

Professor Kipping kindly suggested to us a modification of this method which gives good results. After the cyanohydrin was hydrolysed, water was added, and the acetophenone removed by distillation in steam. The hot acid solution was then filtered and cooled, when atrolactinic acid separated. A further quantity can be obtained by extracting the filtrate with ether. In employing this method, it should, however, be borne in mind that sufficient water must be added after the hydrolysis of the cyanohydrin, and

that the subsequent heating in the presence of hydrochloric acid should not be unduly prolonged, otherwise the atrolactinic acid may be partly converted into atropic acid. Ladenburg and Rügheimer (*loc. cit.*) have pointed out that when atrolactinic acid is boiled under a reflux condenser with moderately dilute hydrochloric acid for some time, then diluted with water, and distilled, small quantities of atropic acid pass over with the steam. With more concentrated hydrochloric acid, appreciable quantities of *iso*atropic acid are formed.

Preparation of Atropic Acid.

The process of Ladenburg and Rügheimer, to which reference has just been made, is not a convenient one for the preparation of atropic acid in quantity. Moreover, the method described by Kraut (*Annalen*, 1863, **128**, 282; compare also Fittig and Wurster, *Annalen*, 1879, **195**, 147), whereby atropine is boiled with barium hydroxide, is not very practical when the expense of atropine is considered, and the same criticism may be passed on Lossen's method of heating atropine with fuming hydrochloric acid at 120—130° (*Annalen*, 1866, **138**, 132).

We found that atrolactinic acid can be converted into atropic acid by distillation under diminished pressure. Atrolactinic acid contains water of crystallisation, but it is not necessary to dehydrate the acid before submitting it to distillation. The method is a convenient one, but certain precautions require to be taken in order to secure a good yield. The chief difficulty arose from the ease with which atropic acid is transformed under the agency of heat into α- and β-*iso*atropic acids (Fittig and Wurster, *loc. cit.*). We carried out the distillation in a silica flask with a capacity of 110 c.c. and provided with a side-tube of 12 mm. internal diameter and 28 cm. in length. The side-tube acts as a suitable condenser, and there is no danger of it becoming choked owing to the solidification of the condensed atropic acid, as is the case when an ordinary distilling flask is used. Experience showed that it is very advisable to heat the atrolactinic acid with a free flame rather than to use an oil-bath. If the distillation is carried out too slowly, a viscous residue of the *iso*atropic acids is left in the distilling flask, and the yield of atropic acid is poor. On the other hand, if the operation is conducted too rapidly, some atrolactinic acid passes over along with the atropic acid; the two acids are, however, easily separated by taking advantage of their very different solubilities in water, atropic acid dissolving, according to Kraut, in 692·5 parts of water at 19·1°, whilst the solubility of

trolactinic acid was found by Lennart Smith (*J. pr. Chem.*, 1911, ii], **84**, 737) to be 17·04 parts per litre of water at 18°. Under a pressure of 10—15 mm., an oil distils at 177—179° and solidifies quickly. The distillate is dissolved in a warm mixture of ethyl alcohol and water, and hot water is then added until the liquid becomes cloudy. The atropic acid separates on cooling in the form of iridescent leaflets. Should the melting point of the dried crystals indicate that the atropic acid is not quite pure, the crystals are left for some time in contact with water in order to remove atrolactinic acid.

The results of three experiments may be given:

(1) Nineteen grams of dehydrated atrolactinic acid gave 12 grams of atropic acid.

(2) Twenty grams of dehydrated atrolactinic acid gave 13 grams of atropic acid.

(3) Twenty-one grams of dehydrated atrolactinic acid gave 13·5 grams of atropic acid.

The time of distillation was fifteen minutes. The mean yield from the above figures is 72 per cent. of the theoretical; a further small quantity of atropic acid may be obtained from the mother liquors.

The acid melts at 106—107°. It gave $C = 73·0$; $H = 5·5$. (Calc.: $C = 73·0$; $H = 5·4$ per cent.)

This is a much more practical method for preparing atropic acid than that described by Ladenburg and Rügheimer (*Ber.*, 1880, **13**, 2041), who also used acetophenone as the starting point. They formed acetophenone dichloride, $CMePhCl_2$, which, by means of potassium cyanide and ethyl alcohol, was converted into the nitrile, $CMePh(CN)\cdot OEt$, and this, on hydrolysis by baryta, gave the barium salt of ethyl atrolactinic acid, $CMePh(CO_2H)\cdot OEt$. Atropic acid was obtained from the latter acid by treatment with concentrated hydrochloric acid. The method now described is also more practical than Spiegel's method, whereby atropic acid is produced by boiling β-chlorohydratropic acid with aqueous sodium hydroxide.

Preparation of β-Chlorohydratropic Acid.

An interesting study of the additive compounds of atropic acid and the halogen acids is described by Merling, who obtained β-chlorohydratropic acid by heating atropic acid with fuming hydrochloric acid in a sealed tube at 100° for five hours (*Annalen*, 1881, **209**, 1). The yield of the chloro-acid is not stated, but it is certain that the method is not a practical one, as atropic acid

would, under the experimental conditions, undergo considerable transformation into the *isoatropic* acids, and the formation of these acids is indicated in Merling's description.

The following is a convenient method for preparing β-chloro-hydratropic acid. Ten grams of atropic acid were dissolved in 200 c.c. of dry ether free from alcohol, and a current of dry hydrogen chloride was passed in slowly for about two hours. The solution was kept warm during this period, the flask containing it having been attached to a reflux condenser provided with a calcium chloride drying tube. The solution was then kept overnight, and the hydrogen chloride again passed through the warm solution next day for four to five hours. After the bulk of the ether was removed by distillation, the residual liquid was allowed to evaporate spontaneously. An almost completely solid residue was obtained which, after two crystallisations from carbon disulphide, was sufficiently pure for analysis. Only one crystallisation is necessary when the chloro-acid is to be used for conversion into tropic acid. The acid melted at 88—89°, whereas Merling gives 87—88°. (Found : Cl = 19·3. Calc. : Cl = 19·2 per cent.)

Ten grams of atropic acid gave 10 grams of the chloro-acid, a yield of 80 per cent. of the theoretical.

Conversion of β-Chlorohydratropic Acid into Tropic Acid.

Merling (*loc. cit.*) found that the chloro-acid could be hydrolysed by heating with a solution of potassium carbonate. The present authors have examined the hydrolysis under various conditions with the object of securing as good a yield of tropic acid as possible, since certain secondary reactions are liable to occur. These reactions are (*a*) the tendency for the formation of styrene through the elimination of hydrogen chloride and carbon dioxide, as observed by Merling, and (*b*) the readiness with which tropic acid in the presence of alkalis loses water and passes into atropic acid (Hesse, *J. pr. Chem.*, 1901, [ii], **64**, 286). The action of water alone was found to be unsatisfactory, but better results were obtained with aqueous sodium carbonate. The amount of sodium carbonate used was rather less than would be required to neutralise the original acid and the hydrochloric acid formed during the hydrolysis; there was practically no difference in the yield whether all the sodium carbonate was added at the beginning or gradually during the time of boiling. As an example, the following experiment may be quoted.

Four grams of the chloro-acid were mixed with 80 c.c. of water, and the mixture was boiled under a reflux condenser. A solution

of sodium carbonate (1·73N) was run in slowly, the boiling being maintained; 24·1 c.c. were added in the course of fifteen minutes, the boiling being then continued for a further three and a-half hours without the addition of any further quantity of alkali. On cooling, the solution was faintly alkaline; it was extracted with ether to remove styrene, acidified with dilute sulphuric acid, and extracted five times with ether. The ethereal solution was dried with sodium sulphate, and to the oily residue which remained after the removal of the ether, benzene was added. The resulting crystals were separated, washed with benzene, and dried. The yield was 2·32 grams and the melting point 116—117°. The aqueous solution which had been extracted with ether gave an additional 0·2 gram of tropic acid when extracted for five hours in a continuous extractor. Yield = 70 per cent. Equivalent: Found: 166·6. Calc.: 166·1.

The residue obtained by the evaporation of the benzene filtrates reduced alkaline permanganate strongly, and doubtless consisted of a mixture of atropic and tropic acids.

In a similar experiment, using 10 grams of the chloro-acid, the yield of tropic acid amounted to 61 per cent. of the theoretical.

The tropic acid obtained in this manner was free from atropic acid.

The yield was smaller when sodium hydroxide was used in place of sodium carbonate. Solutions of sodium acetate and silver nitrate were also employed as hydrolysing agents, but in neither case was the yield of tropic acid so good as when sodium carbonate was used.

Attempts were made to study the hydrolysis from the kinetic point of view, but for various reasons these proved unsuccessful. At the boiling point, the reaction takes place too rapidly to permit of accurate determinations of the velocity of reaction, whilst at lower temperatures the solubility of the acid in water is too small. An attempt was made to overcome the latter difficulty by using a mixture of alcohol and water as the solvent, but under these conditions the velocity of reaction was reduced to such small dimensions as to be impossible of accurate determination.

Attempts to Reduce Chlorotropic Acid.

The method described by Ladenburg and Rügheimer for the preparation of chlorotropic acid was followed. The chlorotropic acid obtained melted at 129—130°, in agreement with the value given by Ladenburg, namely, 128—130°.

Reference has already been made in the theoretical portion of

the paper to the failure which attended our numerous efforts to reduce chlorotropic acid to tropic acid. Ladenburg describes the action as taking place when zinc dust and iron filings are added to a solution of the acid in a concentrated aqueous solution of potassium hydroxide, but no information is given regarding the actual concentration of the alkali he used. We made numerous experiments, using alkaline solutions of different concentrations. When the chlorotropic acid was dissolved in a solution of sodium or potassium hydroxide containing 20 grams of alkali in 100 c.c. of water and left for several days in contact with zinc dust and iron filings, the product which was obtained after the removal of the dissolved zinc and the extraction of the acidified portion by means of ether was a substance of indefinite melting point, and still contained chlorine. With a more concentrated solution of alkali (10 grams of potassium hydroxide in 10 grams of water), the product was free from chlorine. It appeared to be a mixture, as it had a strong reducing action on alkaline permanganate, but on treatment with benzene, part of it was sparingly soluble, and this, after washing with benzene, was practically devoid of reducing action. It was soluble in water, melted at 144—146°, and was probably atroglyceric acid, which melts, according to Fittig and Kast (*Annalen*, 1881, **206**, 32), at 146°.

Other reducing agents which were tried were sodium amalgam, zinc and hydrochloric acid, sodium hydroxide and aluminium powder, and aluminium amalgam. In each case, chlorotropic acid was recovered.

Preparation of the Optically Active Tropic Acids.

85·4 Grams of hydrated quinine (1 mol.) were dissolved in 850 c.c. of absolute ethyl alcohol at 17°, and 37·5 grams of *r*-tropic acid (1 mol.) were added with stirring until the solution was homogeneous. Crystallisation began after five minutes, and proceeded rapidly. After nineteen hours at the ordinary temperature, the crystals were separated; after remaining on a porous plate for three days, they amounted to 71 grams. Crystallisation was carried out another eight times from ethyl alcohol. The alcohol was distilled off from the filtrate from each successive crystallisation, the residue decomposed by dilute sulphuric acid, and the tropic acid extracted with ether and dried with sodium sulphate. The progress of the resolution was indicated by determining the specific rotatory power of the successive acids in ethyl-alcoholic solution, the following values for $[\alpha]_D$ being obtained: $-54·2°$ $-36·7°$, $-6·1°$, $+23·1°$, $+41·2°$, $+60·8°$, $+67·1°$, $+69·4°$

+ 69·6°. The quinine d-salt amounted to 25·5 grams; it separated from ethyl alcohol in felted leaflets grouped in rosettes melting at 190—191°; 100 c.c. of its ethyl-alcoholic solution contain about 0·55 gram of the salt at 13°. The salt was decomposed by dilute sulphuric acid, and the tropic acid repeatedly extracted with ether, 7·2 grams of pure d-acid being obtained.

d-*Tropic acid* is sparingly soluble in benzene, from which it separates in lustrous needles melting at 128—129°. It crystallises from water in glassy needles and plates grouped in rosettes:

0·1858 gave 0·4421 CO_2 and 0·1043 H_2O.   C = 64·9; H = 6·3.

$C_9H_{10}O_3$ requires C = 65·0; H = 6·1 per cent.

Its specific rotation was determined in the following solvents:

(*a*) Ethyl alcohol:

$$c = 2·695,\ l = 2\ ;\ a_D^{16}\ +3·89°\ ;\ [a]_D^{16}\ +72·2°.$$

(*b*) Water:

$$c = 1·515,\ l = 2\ ;\ a_D^{16}\ +2·43°\ ;\ [a]_D^{16}\ +80·2°.$$

(*c*) Acetone:

$$c = 2·19,\quad l = 2\ ;\ a_D^{13}\ +3·67°\ ;\ [a]_D^{13}\ +83·8°.$$

For the preparation of the l-isomeride, 9 grams of acid with $a_D -54·2°$ for $c = 2·65$ in ethyl-alcoholic solution, and 4 grams of acid with $[a]_D -36·7°$ for $c = 2·574$ in ethyl-alcoholic solution obtained from the first two filtrates in the resolution just described), were united and added to a warm solution of 23·8 grams of morphine in 350 c.c. of ethyl alcohol. On cooling, glassy crystals began to separate, and these were collected on the following day. The product, dried in air at the ordinary temperature, amounted to 32·5 grams. It was crystallised from ethyl alcohol six times. The tropic acid recovered from the mother liquors from these crystallisations gave the following values for $[a]_D$ in ethyl-alcoholic solution: −13·5°, −28°, −56°, −59·4°, −60·7°, −63°. Although the morphine salt (14 grams) was not yet quite pure, it was deemed advisable at this stage to decompose it with dilute sulphuric acid. The resulting acid (4 grams) was nearly pure, giving the value $[a]_D -71·3°$ in ethyl-alcoholic solution. The pure acid was obtained after one crystallisation from water.

l-*Tropic acid* melts at 128—129°. Equivalent: Found: 166·5. Calc.: 166·1. The values for its rotatory power were determined in the following solvents, and are in agreement with the corresponding values for its d-isomeride:

(*a*) Ethyl alcohol:

$$c = 2·578,\ l = 2\ ;\ a_D^{17}\ -3·74°\ ;\ [a]_D^{13}\ -72·5°.$$

(b) Water:

$$c = 1\cdot538, \ l = 2 \ ; \ a_D^{15} - 2\cdot43^\circ ; \ [a]_D^{15} - 79\cdot0^\circ.$$

(c) Acetone:

$$c = 1\cdot806, \ l = 2 \ ; \ a_D^{15} - 3\cdot01^\circ ; \ [a]_D^{15} - 83\cdot3^\circ.$$

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LXVIII.—*The Absorption Spectra of the Nitric Esters of Glycerol.*

By HARRY HEPWORTH.

In 1906, Kast (*Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1906, 1, 225) discovered that nitroglycerin or glyceryl trinitrate is capable of existing in two isomeric forms in the solid state, a labile isomeride melting at 2·8° and a stable form melting at 13·5°. In a later paper on this subject by Nauckhoff (*ibid.*, 1911, 6, 124), in which a description of the crystalline structure of the isomeride of higher melting point is given, the author differs from Kast in being unable to isolate the isomeride of lower melting point. The question of the existence of a second solid form of nitroglycerin has been carefully investigated by Hibbert ("Eighth International Congress of Applied Chemistry," 1912, 4, 37), who has not only confirmed the existence of two solid isomerides, but has also investigated the various conditions under which each may be obtained.

Hibbert has compared these two solid isomerides with the two isomeric forms of benzophenone, and although he justly points out that structural isomerism is theoretically possible, yet on the whole the evidence points to the two forms of nitroglycerin being physical isomerides one of the other. This conclusion is largely based on the views of Schaum (*Annalen*, 1898, 300, 209), according to whom the criterion between chemical and physical isomerism is to be found in the fact that with purely physical isomerides, inoculation of the solid labile with the solid stable form brings about the complete conversion of the former in the absence of any solvent.

Now it is evident that if the two solid forms of nitroglycerin are to be represented by two different structural formulæ, then the labile and stable forms should give rise to two different chemical compounds, either in the liquid state or in solution, and it is reasonable to suppose that these solutions will exhibit different absorption spectra. Aqueous solutions of nitroglycerin derived from the two forms have been examined spectrographically, and found to give identical spectra (Fig. 1), from which it is clear that there is no evidence of chemical isomerism in solution, and that the labile and solid forms of nitroglycerin are to be regarded as physical isomerides. Since the nitroglycerins examined showed general absorption only, it is improbable that an equilibrium mixture of dynamic isomerides is obtained when either form is dissolved in water.

The absorption spectrum of a sample of commercial nitroglycerin has also been determined as a matter of interest. It will be observed (Fig. 1) that the latter is much more absorptive than pure nitroglycerin. This cannot be due to the presence of lower nitrates, as the latter are soluble in water.

The lower nitrates of glycerol have been investigated by Will (*Ber.*, 1908, **41**, 1107), and the glyceryl $\alpha\beta$- and $\alpha\gamma$-dinitrates were prepared and separated as described by him. It is evident that in the case of the dinitrates, the two isomerides may have the structural formulæ

$$
\begin{array}{ccc}
CH_2 \cdot OH & & CH_2 \cdot O \cdot NO_2 \\
| & & | \\
CH \cdot O \cdot NO_2 & \text{and} & CH \cdot OH \\
| & & | \\
CH_2 \cdot O \cdot NO_2 & & CH_2 \cdot O \cdot NO_2
\end{array}
$$
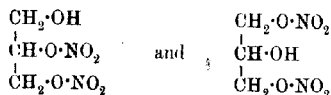
and should therefore give rise to two different absorption spectra. The absorption in aqueous solution was investigated, with the results shown in Fig. 2. It will be observed that the $\alpha\beta$-ester shows the stronger absorption, and this would be expected from the fact that this ester is more unsymmetrical than the $\alpha\gamma$-dinitrate. Both isomerides show less absorption than nitroglycerin.

A sample of α-methylin dinitrate was kindly provided by Mr. D. T. Jones, and had been prepared by the nitration of glyceryl α-monomethyl ether (Jones, T., 1919, **115**, 76). This sample had a faint yellow colour, and was fractionally crystallised before use. The absorption spectrum is shown in Fig. 2, and it will be observed that it is slightly more absorptive than glyceryl $\alpha\beta$-dinitrate.

Glyceryl α- and β-mononitrates were prepared by extracting the neutralised, concentrated mother liquors left after the extraction of the dinitrates, as described by Will (*loc. cit.*).

The absorption spectra of glyceryl α- and β-mononitrates in aqueous solution are shown in Fig. 3. The α-compound prepared
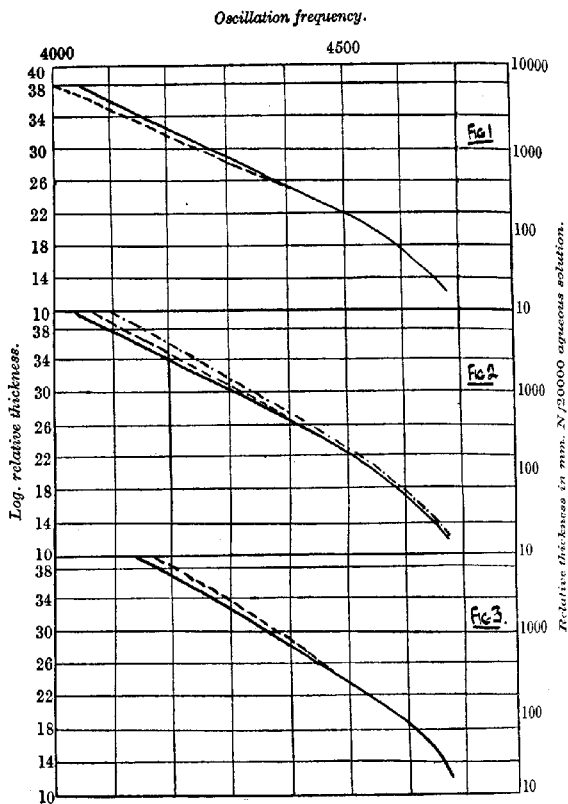
FIG. 1.—*Nitroglycerin* $\left\{ \begin{array}{l} \text{————— } \textit{Labile or stable form.} \\ \text{- - - - } \textit{Commercial nitroglycerin.} \end{array} \right.$

FIG. 2.— $\left\{ \begin{array}{l} \textit{a-Methylin dinitrate} \text{ ————} \\ \textit{Glyceryl aβ-dinitrate} \text{ - - - -} \\ \textit{Glyceryl aγ-dinitrate} \text{ - · - · -} \end{array} \right.$

FIG. 3.— $\left\{ \begin{array}{l} \textit{Glyceryl a-mononitrate} \text{ ————} \\ \textit{Glyceryl β-mononitrate} \text{ - - - -} \end{array} \right.$

by Nef's method gave a spectrum almost identical with that prepared by the direct nitration of glycerol. It will be observed that

both isomerides exhibit less absorption than either the isomeric dinitrates or the trinitrate, and that the unsymmetrical α-isomeride is rather more absorptive than the symmetrical β-isomeride.

The absorption spectrum of glycerol does not appear to have been investigated, and a sample of Hehner's glycerol, used as the standard in the chemical analysis of glycerol used for dynamite, and guaranteed to contain no impurity except water, was examined after drying over phosphoric oxide in a vacuum for four days. It was found that a normal aqueous solution was quite diactinic through a thickness of 10 mm.

It is therefore evident that the substitution of a hydrogen atom of one of the hydroxyl groups of glycerol by a nitro-group produces a profound change in the absorption spectrum, whereas the substitution of one or both hydrogen atoms of the remaining hydroxyl groups by nitro-groups, whilst increasing the general absorption, does not produce nearly so great a change in the absorption spectrum.

EXPERIMENTAL.

Preparation of Pure Nitroglycerin (Glyceryl Trinitrate).

One hundred and eighty grams of Prices's double distilled glycerol were nitrated with a clear, mixed acid of the composition:

	Per cent.
Nitric acid	40·0
Sulphuric acid	57·68
Nitrous acid	0·18
Water	2·14

The nitration was carried out in a large beaker surrounded by a freezing mixture, the glycerol being added at such a rate as to keep the temperature at 10—12° throughout the nitration. The ratio of acid to glycerol was about 7:1. Air stirring was continued for ten minutes after the whole of the glycerol had been added, after which the nitroglycerin was allowed to separate for thirty minutes, no accelerant being employed.

The lower layer of mixed acid was then run off, and the nitroglycerin washed with twelve successive changes of distilled water at 25—30°, the addition of sodium carbonate or any other stabilising substance being avoided. The nitroglycerin was then successively fractionated five times in a freezing mixture. The last fraction, of about 100 grams, was dried in a vacuum over solid potassium hydroxide, and finally obtained as a clear, mobile, faint yellow oil which, after solidification, melted at 13·1°. (Found: N=18·49. Calc.: N=18·51 per cent. H_2O =nil.)

Isolation of the Labile and Stabile Forms of Nitroglycerin.—
The method adopted for the isolation of the labile and stable
forms of nitroglycerin was similar to that described by Hibbert
(*loc. cit.*). The labile form was isolated by inoculating nitro-
glycerin cooled to −40° with a trace of the labile form obtained
by cooling two to three drops of nitroglycerin mixed with glass
wool to −40°, and stirring vigorously. The operation had to be
repeated three times before the labile form was obtained, but this
was probably due to the fact that the nitroglycerin had been
previously frozen. This form appeared to crystallise in the tri-
clinic system, and melted at 2·0°.

The stable form was readily isolated by allowing the nitro-
glycerin to freeze slowly without inoculation. Large bipyramidal
crystals were obtained which melted at 13·1°.

Both forms were allowed to liquefy in a vacuum desiccator over
solid potassium hydroxide, and used at once for the spectrographic
examination. For the confirmation of the spectrographic results,
fresh samples of the labile and stable solid forms were prepared
and recrystallised before use.

Commercial Nitroglycerin.—This product had been made by
nitrating glycerol (for dynamite) with commercial mixed acid
almost identical in composition with that previously described. A
trace of hydrocarbon oil had been used to accelerate the separation,
and the nitroglycerin had been stabilised by thoroughly washing
with dilute sodium carbonate solution followed by several wash-
ings with water at 30°. The sample was filtered twice and dried
over solid potassium hydroxide in a vacuum desiccator for forty-
eight hours. It possessed a distinct brown colour, melted at 12·5°,
and contained $N = 18·46$ per cent. (measured by the nitrometer).

The material was used in this condition for the investigation of
the absorption spectrum.

a-Methylin Dinitrate.—This was fractionally crystallised three
times and dried in a vacuum over solid potassium hydroxide. The
sample examined spectrographically crystallised in white, mono-
clinic prisms melting at 24·2°, and contained $N = 14·23$ per cent.

Preparation of the Lower Nitrates of Glycerol.—The method
adopted for the preparation of the lower nitrates of glycerol was
on similar lines to that described by Will (*loc. cit.*). Two hundred
grams of glycerol were nitrated with a clear, mixed acid of the
composition :

		Per cent.
Nitric acid	....	21·76
Nitrous acid	....	0·06
Sulphuric acid	....	68·22
Water	....	9·96

The nitration was conducted exactly as described under the preparation of trinitroglycerin. On allowing the mixture to remain, about 50 grams of nitroglycerin were separated, after which the mixed acid containing the lower nitrates and a little nitroglycerin was diluted and repeatedly extracted with ether after removing a little nitroglycerin which separated on dilution.

The crude dinitrates were twice washed with a little water, filtered, and partly dried. The αβ- and αγ-dinitrates were separated as described by Will (*loc. cit.*), except that glass wool was used in place of kieselguhr.

The crude αγ-dinitrate was purified by repeated fractional crystallisation, and about 30 grams were finally obtained in large, water-white, prismatic crystals which melted at 26°. On desiccating over calcium chloride in a vacuum for three days, a pale yellow oil was obtained containing $N = 15.30$ per cent., and this was identical with the " dinitroglycerin K " described by Will.

The crude αβ-dinitrate showed no tendency to crystallise when cooled at $-20°$ overnight, but, on inoculation, a little αγ-dinitrate separated. This was repeated until no further traces of the αγ-dinitrate separated, after which it was dried over calcium chloride in a vacuum. The αβ-dinitrate was obtained in this way as a dark yellow oil containing $N = 15.22$ (Calc.: $N = 15.38$ per cent.).

Both dinitrates were kept in a vacuum over solid potassium hydroxide until the solutions were made up for spectrographic examination.

The mononitric esters of glycerol were obtained by evaporating the neutralised mother liquors left after the extraction of the dinitrates, as described by Will (*loc. cit.*). The crude mixture of α- and β-nitrates was easily crystallised by cooling to $-20°$ and vigorously rubbing with a glass rod. Traces of dinitrate were removed from this crude product by dissolving in water and extracting with ether. The separation of the two nitrates was effected by repeatedly washing with a little ether cooled to $-20°$, when it was found that the β-mononitrate was rather more readily soluble than the α-isomeride.

Both forms were obtained in fine leaflets which, after recrystallising twice from water, gave the following results on analysis:

	M. p.	Found N_2 per cent.	Theoretical.
α-Mononitrate.........	57°	10·2	10·2
β-Mononitrate.........	54°	10·13	

Glyceryl α-Mononitrate prepared from Epichlorohydrin.—A sample of the α-mononitrate was prepared from epichlorohydrin, as described by Nef (*Annalen*, 1904, **335**, 238). It was found that

the conversion of epichlorohydrin into epi-iodohydrin, and the latter into glycide nitrate, proceeded quite normally.

Fifty grams of glycide nitrate were heated at 100° with 40 grams of water for four hours. The product was dried in a vacuum over sulphuric acid, and the crude product melted at 54°. It was purified by recrystallisation from ether, this process being repeated three times, when 40 grams of glyceryl α-mononitrate were obtained. The product melted at 57·5° and crystallised in small, white prisms. When mixed with an equal quantity of the α-mono-nitrate, prepared by the direct nitration of glycerol, the mixture melted at 58°.

Unsuccessful attempts were made to prepare the α-mononitrate by the direct nitration of glycide, as described by Hanriot (*Ann. Chim. Phys.*, 1879, [v], **17**, 118), but only a very small yield of the α-mononitrate was obtained.

Spectrographic Examination.—The instrument used was a Hilger quartz spectrograph, size C, fitted with a wave-length scale. The iron arc was used as the source of illumination, and the wave-length scale was standardised against the zinc and copper arcs.

All observations were conducted in aqueous solution, the water employed being diactinic up to 2100 Å.U.

Summary.

From an examination of the absorption spectrum of glycerol and its nitric esters, it is evident that:

(1) The labile and stable forms of nitroglycerin are physical isomerides, and both forms are identical in aqueous solution.

(2) Commercial nitroglycerin is more absorptive than pure nitro-glycerin.

(3) The order of increasing absorption in aqueous solution is β-mononitrate, α-mononitrate, αγ-dinitrate, αβ-dinitrate, and tri-nitrate.

(4) α-Methylin dinitrate is rather more absorptive than glycerol αβ-dinitrate.

(5) The displacement of a hydrogen atom of one of the hydroxyl groups of glycerol by a nitro-group produces a much more profound change in the absorption spectrum than the displacement of one or both hydrogen atoms of the remaining hydroxyl groups.

(6) There does not appear to be any numerical proportionality between the number of hydrogen atoms of the hydroxyl groups displaced by nitro-groups and the degree of absorption for any particular dilution.

The author is indebted to Mr. P. A. Baldock, M.Sc., for confirmation of some of the results described in this paper, and also to the Research Committee of Messrs. Nobel's Explosives Co., and particularly to Messrs. Rintoul and Cowie, for the facilities accorded to him for the carrying out and publication of this work.

LXIX.—The Interaction of Acetylene and Mercuric Chloride.

By DAVID LEONARD CHAPMAN and WILLIAM JOB JENKINS.

ALMOST forty years ago, M. Kutscheroff (Ber., 1881, **14**, 1532, 1540) made the important discovery that hydrocarbons of the acetylene series unite with water in the presence of mercury salts being thereby converted into aldehydes and ketones.

$$CH{:}CH + H_2O = CH_3{\cdot}CHO.$$
$$CH_3{\cdot}C{:}CH + H_2O = CH_3{\cdot}CO{\cdot}CH_3.$$
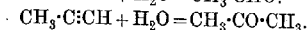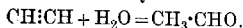
As is well known, the reaction is of special importance, since it is now employed on a commercial scale for the preparation of acetaldehyde, which is subsequently converted by oxidation into acetic acid.

The mechanism of the action of acetylene on mercury salts in the presence of water and aqueous solutions of acids has been studied by Keiser (Amer. Chem. J., 1893, **15**, 537), K. A. Hofmann (Ber., 1898, **31**, 2217; 1899, **32**, 870; 1904, **37**, 4459), Biltz and Mumm (Ber., 1904, **37**, 4417), Biltz (Ber., 1905, **38**, 133), Biginelli (Ann. Chimica, 1898, 16), and Brame (T., 1905, **87**, 427).

Keiser, Hofmann, and Biltz and Mumm investigated the white precipitate obtained by passing acetylene into an aqueous solution of mercuric chloride. Keiser assigned to this substance the formula $ClHg{\cdot}C{:}C{\cdot}HgCl$, which is probably not correct. Hofmann considers that the first product to be formed is a substance having the constitutional formula $\underset{\displaystyle Hg}{(ClHg)_2C\!\!-\!\!CCl_2}$, this being rapidly hydrolysed to trichloromercuriacetaldehyde, $(ClHg)_3C{\cdot}CHO$. Biltz and Mumm have shown that the white precipitate almost certainly has the constitution of trichloromercuriacetaldehyde, but they regard the evidence for the formation of the intermediate compound assumed by Hofmann as unsatisfactory.

Brame has pointed out that both Hofmann and Biltz failed to notice that Biginelli had observed the formation of small quantities of another substance having the constitution $ClHg·HC:CHCl$. By the action of acetylene on a solution of mercuric chloride in dilute hydrochloric acid, Brame has prepared the compound in crystalline form and in sufficient quantity to demonstrate some of its properties. He concludes that there seems good reason for believing that the first action of acetylene on either aqueous or dilute acid solutions of mercuric chloride is the formation of the compound $ClHg·HC:CHCl$ by direct addition, together with acetaldehyde. He adds, however, that it remains to be proved whether this additive compound is an intermediate product concerned in the production of acetaldehyde or whether it is a secondary substance derived from the aldehyde.

The chief product of the action of acetylene on a solution of mercuric chloride in dilute hydrochloric acid is acetaldehyde, and it is therefore unlikely that Biginelli and Brame succeeded in converting more than a small proportion of the acetylene into the additive compound of mercuric chloride and acetylene, and it was no doubt chiefly for this reason that Brame was loth to conclude that it was an intermediate compound concerned in the production of acetaldehyde. His reluctance to draw this conclusion may also have been due to his observation that although the crystals were only sparingly soluble in water, they did not begin to separate from the mercuric chloride solution until the acetylene had been acting on the latter for several hours.

We have recently discovered a method whereby a large proportion of the mercuric chloride can be converted into a crystalline compound of the composition $HgCl_2,C_2H_2$. From 72 grams of mercuric chloride, 50 grams of the additive compound were obtained. Unlike the other mercury compounds obtained by the action of acetylene on the salts of mercury, it is dissolved by most organic solvents. In ether or benzene it is very readily soluble, and can be purified by crystallisation from either of these solvents. It is also unique in having a low melting point. In this respect it resembles the mercury alkyl and mercury alkyl haloid compounds, a circumstance that lends support to the view that the constitutional formula of the compound is either

$$ClHg·HC:CHCl \quad or \quad \begin{matrix} ClHC\!\!-\!\!\!-\!\!CHCl \\ \diagdown\diagup \\ Hg \end{matrix} \quad .$$
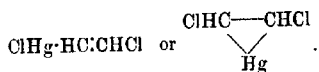
The acetylene was prepared from calcium carbide, and was collected in two gas-holders of 18 litres capacity. The gas was

circulated for eighteen hours through a saturated solution of mercuric chloride in absolute alcohol (72 grams of mercuric chloride in 75 c.c. of absolute alcohol) through which a slow current of dry hydrogen chloride had been passed for five minutes. After sixteen hours, long, colourless, needle-shaped crystals were deposited in the solution. At the end of the experiment these were collected by the aid of the pump. The mass of the crystals was 10 grams. On pouring the solution into a large volume of water, 40 grams of a white solid were precipitated. This was soluble in ether or benzene; it was crystallised from the latter solvent, and proved to be the same substance as the crystals which had separated from the alcoholic solution during the experiment.

An analysis of the product furnished the following results:

Found: $C = 7.93$; $H = 0.693$; $Cl = 23.67$. $Hg = 68.76$.

$C_2H_2,HgCl_2$ requires $C = 8.07$; $H = 0.677$; $Cl = 23.83$; $Hg = 67.42$
per cent.

Owing to decomposition, the melting point could not be accurately determined. It was in the neighbourhood of 113°.

An attempt was made to prepare the compound by passing acetylene through an ethereal solution of mercuric chloride in which dry hydrogen chloride had been dissolved. The acetylene was circulated for twenty hours. At the end of the experiment, the ether was distilled off from the resulting solution, and the solid residue examined. It was almost completely soluble in water, and practically none of it was dissolved in benzene. Therefore the solid residue was almost entirely unchanged mercuric chloride, and very little, if any, of the additive compound could have been formed. It seems likely, therefore, that the compound $HgCl_2,C_2H_2$ is only produced when acetylene is passed into solutions of mercuric chloride in ionising solvents, the compound being formed by the direct addition of the ions $HgCl^{·}$ and Cl' to the unsaturated hydrocarbon.

From the above experiments, it seems probable that the first product of the interaction of acetylene and mercuric chloride is a compound having the constitutional formula $ClHg·HC:CHCl$. The most interesting property of the compound is its solubility in dry organic liquids, for this circumstance, and the fact that excellent yields of it can now be obtained, suggest that it may prove to be a useful reagent in organic synthesis.

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LXX.—*The Basic Properties of Phenanthraquinone.*

By JOSEPH KNOX and HELEN REID WILL.

THE investigation of the basic properties of phenanthraquinone was undertaken as part of a scheme for the investigation of the basic properties of oxygen in organic compounds in general. The results in the case of organic acids and phenols are given in a paper by Knox and Richards (this vol., p. 508), which contains also references to the earlier literature on the subject.

The method adopted was to determine the solubility of the organic compound in water and in solutions of mineral acids of increasing concentration. Increasing solubility of the organic compound with increasing concentration of the acid solution is taken to indicate salt-formation in solution. The salt-formation is assumed to be due to the formation of compounds of the oxonium type by the passage of the oxygen from the bivalent to the quadrivalent condition, as explained in the previous communication (*loc. cit.*).

A red, crystalline nitrate of phenanthraquinone is described by Kehrmann and Mattisson (*Ber.*, 1902, **35**, 343), who ascribe to it

the constitution $\begin{array}{c} C_6H_4 \cdot C:O \\ C_6H_4 \cdot C:O \end{array} \Big\langle \begin{array}{c} H \\ O \cdot NO_2 \end{array}$. They also obtained a red,

crystalline compound of phenanthraquinone with sulphuric acid, which, however, was not analysed. They assume that the dark green solution obtained when phenanthraquinone is dissolved in concentrated sulphuric acid contains a salt in which each oxygen atom of the phenanthraquinone is combined with a molecule of sulphuric acid, whilst the red, crystalline compound is regarded as analogous to the nitrate.

In the present investigation, the solubility of phenanthraquinone in water and in various concentrations of sulphuric, hydrochloric, and nitric acids has been determined at 25°. In order that the solubility determinations in the various acids should be comparable, the following method was chosen. A weighed quantity of pure, powdered phenanthraquinone was placed in a glass-stoppered flask and 200 c.c. of the acid solution were added. The flask was allowed to remain in the thermostat at 25° for several days, with frequent shaking, until the solution was saturated. Each concentration of acid was shaken with phenanthraquinone for varying periods until constant results were obtained. The undissolved phenanthraquinone was then rapidly filtered through a tared Gooch crucible,

washed with cold water until free from acid, dried at 100°, and weighed. The solubility in water was determined by shaking at 25° until saturated and evaporating a litre of the saturated solution to dryness on the water-bath and weighing. The following are the results of the solubility determinations. The concentration of the acid solution is given in gram-equivalents per litre and of the phenanthraquinone in grams per litre.

Solubility of Phenanthraquinone in Sulphuric Acid at 25°.

Conc. H_2SO_4	0·00	5·97	6·19	7·00	9·48	11·6	13·7
Conc. $C_{14}H_8O_2$	0·0075	0·0080	0·0085	0·0095	0·012	0·019	0·030

Conc. H_2SO_4	15·1	17·1	18·6
Conc. $C_{14}H_8O_2$	0·043	0·082	0·116

Solubility of Phenanthraquinone in Hydrochloric Acid at 25°.

Conc. HCl	0·00	3·11	4·25	5·12	6·05	6·07	7·20
Conc. $C_{14}H_8O_2$	0·0075	0·012	0·016	0·023	0·029	0·031	0·046

Conc. HCl	8·50	9·25	10·8
Conc. $C_{14}H_8O_2$	0·058	0·088	0·157

Solubility of Phenanthraquinone in Nitric Acid at 25°.

Conc. HNO_3	0·00	4·26	4·54	5·02	6·15	6·66	6·70
Conc. $C_{14}H_8O_2$	0·0075	0·049	0·053	0·067	0·099	0·114	0·118

Conc. HNO_3	7·20	7·45	8·30
Conc. $C_{14}H_8O_2$	0·157	0·175	0·227

These results are shown graphically in the diagram, in which the ordinates represent the concentration of the phenanthraquinone in centigrams per litre and the abscissæ the concentration of the acid in gram-equivalents per litre.

A high degree of accuracy is not claimed for these solubility determinations. They are, however, sufficiently accurate to show that in every case the solubility increases with increasing concentration of the acid, indicating that phenanthraquinone has basic properties. For the reasons given by Knox and Richards (*loc. cit.*), these basic properties are attributed to the formation of salts of the oxonium type, in which the oxygen becomes quadrivalent.

The increase in solubility is greatest in nitric acid and least in sulphuric acid for equivalent concentrations. This was also found to be the case with organic acids and phenols (*loc. cit.*), so that salt-formation occurs most readily with nitric acid and least readily with sulphuric acid.

An attempt was made to determine the concentration of nitric

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acid which is in equilibrium with phenanthraquinone and the nitrate, $C_{14}H_8O_2,HNO_3$, according to the reversible reaction

$$C_{14}H_8O_2 + HNO_3 \rightleftharpoons C_{14}H_8O_2,HNO_3.$$
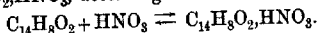
The equilibrium is reached very slowly, however, from the left-hand side. By shaking phenanthraquinone at 25° with various concentrations of nitric acid, it was found that the red nitrate was formed with concentrations of acid in the neighbourhood of 12·5N, but that slightly more dilute acid acted very slowly, as indicated by the very slow fall in concentration of the acid with continued shaking. Even with 12·5N-acid, the concentration of the acid diminished only slightly, although the red compound was obviously present, since the nitrate is formed on the surface of the phen-

anthraquinone and prevents further action of the acid. The equilibrium was therefore approached from the other side. The red nitrate was prepared by the method described by Kehrmann and Mattisson, and shaken at 25° with various concentrations of nitric acid. When the concentration of nitric acid was below 11·2N, decomposition of the nitrate took place comparatively rapidly until the concentration of the nitric acid rose to this value, provided that sufficient nitrate was added to have both solid phases, phenanthraquinone and its nitrate, present at equilibrium. At 25°, therefore, phenanthraquinone and its nitrate, $C_{14}H_8O_2,HNO_3$, are in equilibrium with 11·2N-nitric acid.
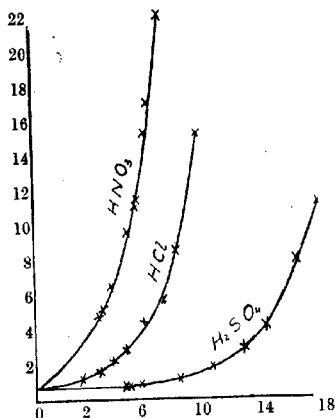
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LXXI.—*The Solubility of Silver Acetate in Acetic Acid and of Silver Propionate in Propionic Acid.*

By JOSEPH KNOX and HELEN REID WILL.

THE solubility of silver acetate was determined at 25° in water and in various concentrations of acetic acid, up to about 17N, in order to see whether an acid salt was formed under these conditions. In the analogous case of sodium acetate and acetic acid, two acid salts, $C_2H_3O_2Na,C_2H_4O_2$ and $C_2H_3O_2Na,2C_2H_4O_2$, are formed (Farmer, T., 1903, **83**, 1440; Vasilieff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 753; Dukelski, *Zeitsch. anorg. Chem.*, 1909, **62**, 114; Abe, *Mem. Coll. Sci. Eng. Kyōtō*, 1911, **3**, 13; Dunningham, T., 1912, **101**, 431). In the case of silver acetate and acetic acid at 25°, the solubility curve is continuous, indicating that no new phase is formed. The solubility of silver propionate in various concentrations of propionic acid was also determined, and a continuous solubility curve also obtained.

The silver salts were purified by recrystallisation from water, and shown by analysis to be pure. Excess of the salt was shaken with water or varying concentrations of the corresponding acid until constant solubility was obtained. The silver salt in solution was determined gravimetrically as silver chloride, and the acid by titration with sodium hydroxide free from carbonate. The experimental results are as follows. The concentration of the silver salt is given in grams per litre, and that of the acid in gram-equivalents per litre.

Solubility of Silver Acetate in Acetic Acid Solutions at 25°.

Conc. $C_2H_3O_2Ag$.									
11·13	10·73	10·32	9·98	9·52	9·19	8·72	8·29	7·73	7·31
Conc. $C_2H_4O_2$ ...									
0·00	1·00	2·00	2·98	4·19	4·98	5·99	6·80	8·01	8·97
Conc. $C_2H_3O_2Ag$.									
6·78	6·15	5·33	4·96	4·29	3·43	2·48	1·09		
Conc. $C_2H_4O_2$ ...									
9·96	11·02	12·32	12·97	13·97	14·96	15·93	17·28		

Solubility of Silver Propionate in Propionic Acid Solutions at 25°.

Conc. $C_3H_5O_2Ag$.								
9·04	8·58	8·01	7·60	6·78	5·78	4·96	3·16	2·17
Conc. $C_3H_8O_2$ ...								
0·00	1·00	2·00	2·97	4·95	6·97	8·56	11·40	13·03

The results of the solubility determinations are shown graphic-ally in the diagram, in which the ordinates represent the concentration of the silver salt in grams per litre and the abscissæ the concentration of the acid in gram-equivalents per litre.

The solubility of silver acetate in water at 25° is given by Gold-schmidt (*Zeitsch. physikal. Chem.*, 1898, **25**, 91) as 11·18 grams per litre, and by Jaques (*Trans. Faraday Soc.*, 1909, **5**, 225) as 11·07 grams per litre. The value obtained by interpolation from
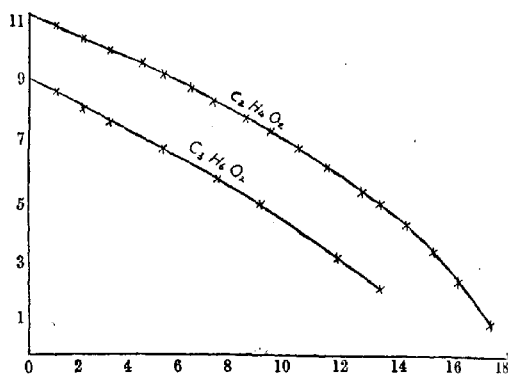
Raupenstrauch's results at 20° and 30°, recalculated to grams per litre, is 11·21 grams (*Monatsh.*, 1885, **6**, 585). For silver pro-pionate in water at 25°, Goldschmidt (*loc. cit.*) gives 9·04 grams per litre, and the same figure is obtained from Raupenstrauch's results (*loc. cit.*). These values for the solubility of silver acetate and silver propionate in water at 25° agree closely with ours.

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Emission Spectra and Atomic Structure.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON
MARCH 6TH, 1919.

By JOHN WILLIAM NICHOLSON.

THE invitation of the Council of the Chemical Society to take part
in a series of three lectures during the present session is peculiarly
acceptable to me, in that it gives me an opportunity to draw
attention to certain problems of atomic structure in which further
progress can scarcely be hoped for without a more complete co-
operation between the physicist and chemist than has hitherto
been customary.

The chemist appeals frequently to the physicist, or even to the
mathematician, for guidance. I wish to emphasise, and I hope
that my remarks will serve to do so, that it is even more a necessity
that the real aid to be invoked in the problem which we share in
common—that of the elucidation of the nature of the elementary
atom—is that of the chemist. It is my belief that this problem
will not proceed further towards a satisfactory solution without
the joint action of the physicist and the chemist, who have hitherto
tended to work in separate channels, without a complete knowledge
of their mutual activities. Some of the problems in which co-
operation is desirable I hope to indicate, perhaps vaguely, but
sufficiently clearly for those of us who have really common interests.

Prof. Soddy has relieved my task very much. One of the
pioneers on the chemical side, he gave an account of the bearing
of chemistry on the problem of atomic structure which is beyond
criticism, and to which nothing further can really be added from
that point of view. Some questions were raised on which more
could perhaps be said—for instance, the spectra of isotopes, to
which I may refer again. As regards his address, I should like
to say at the outset that the views therein expressed cannot be
contested seriously by the physicist or the mathematician who has
worked at the problem of atomic structure.

My own object is to consider this problem from the point of
view of spectra. I will endeavour to confine my remarks to the
more immediate issues, for the subject of spectra is at present so
vast as to transcend any delimitation as a branch of chemistry or
of physics. I must consider it only from the point of view of
atomic structure, which I have already described as the ultimate
aim of both physics and chemistry, an aim only to be achieved by

co-operative effort, and preferably by the existence at the same time of strong chemical and physical schools at one of our leading universities. Prof. Soddy began at the "heavy" end of the periodic table of the elements. I shall, in effect, begin at the "light" end—with hydrogen and helium and possible lighter elements. Before I so begin, however, a few words regarding the nature of spectra are necessary—and my remarks are confined to emission spectra, and not absorption spectra, which, although of supreme importance to the chemist, are less interesting as bearing on the structure of the atom.

Any complete account of the nature of spectral series, as elucidated by experiment, would be quite outside the limits of time of a single lecture. I must perforce neglect various matters, such as satellites of spectrum lines, as of secondary importance. The account of spectra which I give must be accepted as an ideal simplification of existing spectra, to which, nevertheless, theories of atomic structure must conform. Moreover, it is not to be understood that such an account is valid for the heavier elements, the spectra of which exhibit a more complex scheme of relations, but since atomic theories must in practice be illustrated or even confirmed from the lighter and more chemically simple elements, showing the simpler types of spectra, no disadvantage is thereby involved.

Series of spectrum lines will then be regarded as falling into three mutually related sets—the so-called diffuse, sharp, and principal series. The existence of any one of these implies that of the other two, and the lines constituting any one of these series may be single, double, or triple. An element may emit two distinct sets of series, perhaps more. For instance, helium gives three series of single lines and three of doublets. It is a great advantage to work with wave numbers, or numbers of complete wave-lengths in a centimetre, rather than wave-lengths themselves, in the discussion of series, for this procedure enables the relations of the three types of series to be stated very simply. If we proceed along a spectrum series towards the violet, the lines are seen to become closer and closer together until a limit is reached at which two successive members coincide. Lines are never, in fact, visible in the laboratory near this limit, although their convergence towards it can be seen readily enough, the actual limit being a matter of calculation. The diffuse and sharp series tend to the same limit in all cases, and from this limit we can calculate, and thereby predict, the wave-number intervals between the lines of the principal series. The Rydberg-Schuster law gives also the limit of the principal series.

In regard to double lines, the series relations are even more interesting. The wave-number interval between the two members of a doublet is constant along the diffuse and sharp series—the two members form separate series tending to different limits. In a principal series, on the other hand, they tend to the same limit, and the doublets rapidly become narrower towards the violet end of the spectrum.

Our present interest in these questions is mainly confined to the discovery of a chemical atom which can produce a set of ethereal waves the frequencies of which are related in this curious manner.

I will endeavour to summarise some of the more extreme difficulties met at the outset. In the first place, a series contains an infinite number of lines, and if the spectra are in any sense dynamical vibrations of the atom, the frequencies of which are transmitted to our instruments by the ether, the atom must have an infinite number of degrees of freedom. This is not consistent with the very finite number of possible vibrating parts which, from many converging lines of evidence, we are now compelled to assume for its structure—the positive nucleus and some electrons in rotation round it. The only way to surmount this difficulty is, in fact, to postulate that series spectra are derived from the nucleus, and are not a question of the outer electrons. This nucleus must then be endowed with an extremely complex structure. In this way, we might hope to preserve the conception of spectra as dynamical vibrations, and all the lines of the three series might then arise simultaneously from the same atom. We cannot altogether reject this possibility, but if it were more than a possibility, we should be driven to a very disappointing conclusion. For nuclear structure is a thing we may, and often do, speculate about, but it is at the same time practically beyond the power of our experiments. We know, for instance, that α- and β-particles in radioactive phenomena are shot from the nucleus, but nothing we can do appears to have any retarding or accelerating effect on such phenomena or to give a clue to the arrangement of the particles before their emission. We cannot, in fact, influence the nucleus in any effective way, but only its surrounding electrons. Speculative theories of spectra as arising from a nucleus may then be constructed in the future, but there would remain the fundamental difficulty of testing them experimentally. Many phenomena, however, for instance, the Zeeman and Stark effects, and the curious variations shown in the spectra of mixed gases, seem to indicate that the surrounding electrons are vitally concerned and that the nucleus gives us no mode of escape.

Since we cannot have the infinite number of degrees of freedom,

the conception of an infinite number of states of an atom arises with a finite number of spectrum lines—perhaps only one—corre-sponding with each state. Two lines of the same series are then never given simultaneously from the same atom. This underlies the two theories of production of spectra which have achieved some success, namely, the theories of Ritz and Bohr, on which more will be said later.

The second difficulty to which I shall refer is that all the formulæ which give a useful expression for the series relations of spectral lines serve to show quite conclusively that the frequencies of the lines are simple functions of a quantity to which we can assign any whole-number value we please, each value corresponding with a definite line. Dynamical theory always leads to an expression for the *square* of the frequency, and the frequency itself is a square root which ordinarily does not work out into a simple form. This difficulty is of a type which I do not wish to expound at length now, but it is sufficient to say that a satisfactory theory of spectra as atomic vibrations must lead to an equation giving the frequency itself, and not its square, in the first instance. There is only one known case in which this occurs, namely, the case in which the forces which regulate the vibrations of the atomic electrons are mainly *magnetic*. This is the manner in which Ritz overcomes the difficulty. He found it necessary to postulate the existence of a specific magnetic moment—the *magneton*, in fact—which was in-variable, like the electric charge of an electron, from atom to atom. An atom could contain various numbers of magnetons, each corresponding with one of its "states," and each state gave a spectrum line when the electrons of the atom vibrated under the influence of the elementary contained magnets.

This theory of spectra was extraordinarily successful. Its prophecies were verified at every turn, and it was the instrument which, more than any other, has directed the experimental work of spectroscopists into fruitful channels and led to a consolidation of the phenomena of spectra into great generalisations which are now fully established. It led, in fact, to the well-known *com-bination principle* of spectra on which Bohr's theory was subse-quently founded. The defects which are regarded as fatal to it are derived from other considerations than those of spectra. Such problems as the scattering of α- and β-particles by atoms, treated experimentally and compared with the theory developed by Darwin, Bohr, and others, do not appear to be consistent with such fields of magnetic type, although Hicks has had some success in the contrary direction in interpreting the deflections of these particles by a magnetic core of the atom.

I do not propose to say more regarding the existence of magnetic forces within the atom or as regards the existence or non-existence of the magneton itself. There is a vast amount of literature on the subject, which only, in fact, comes into the scope of existing theories of spectra in the manner already briefly indicated. The other theory which has had some success in explaining series spectra is of quite another type, and does not admit such magnetic forces. We shall discuss it later, but shall proceed at present to consider some spectra which do not form ordinary series.

It is difficult to think of an atom as a nucleus of positive electricity with satellite electrons without imagining that the atom is capable of vibrations of a periodic type, and that these vibrations must show themselves in the form of optical wave-lengths. These should, from general considerations, have a frequency which brings many at least into the visible spectrum. The argument is founded merely on the accepted—from many well-established facts —values of the radii, electronic velocities, and so forth. I will proceed to give a short account of some of my own work in this connexion, the data on which it is founded being mainly those of spectroscopic astronomy.

In the first place, one very general result must be stated. It is so frequently ignored in the construction of theoretical atoms that too much emphasis can scarcely be given. Under the inverse square law of attraction or repulsion of elements of electricity, or, indeed, any inverse law at all, coplanar rings of electrons are not possible, in the sense that even an undisturbed atom cannot preserve its configuration. The conclusion may probably be extended to non-coplanar rings.

Rutherford has shown that the nucleus apparently continues to act on electrons with this law at distances less than the atomic radius, and there is much evidence that the electrons continue so to act on each other. If this is confirmed further, the explanations of the phenomena of Röntgen radiation, based on transfer of an electron from one ring to another, will fall to the ground. The subject has many ramifications, and the following statements, capable of logical demonstration, show the chaos in which the physics of the atom is now involved :—

(1) Experiments on scattering of α- and β-particles by atoms indicate that the usual laws of electrical action are valid *inside* the atom. This precludes comparable forces of magnetic origin.

(2) Separate rings of electrons are impossible if (1) is true, and this would annihilate attempts hitherto made to interpret the characteristic X-radiation of atoms, which then can only be a property of the nucleus.

(3) The now accepted dimensions of this nucleus are not consistent with (2). They are also not consistent with the fact that it is capable of sending out β-particles during a radioactive change, for a single β-particle is much larger than a nucleus.

It would be possible to continue such a table of contradictions for a considerable time, and if the quantum theory is invoked, the situation is little better. I do not wish to do more than indicate the position, for more could not be done in a sufficient space. What I wish to make clear is that whilst those who, like Prof. Soddy, discuss radioactive phenomena, proceed from the "heavy" end of the periodic table, any constructive account of spectra must begin at the "light" end.

For the simplest possible elements, there can only be a question of one ring, whatever view is adopted. My own procedure was as follows. Taking the ordinary laws of electrical action, it is possible to work out the frequencies of dynamical vibration of an atom with, say, any number of electrons up to six, in one ring, rotating round a nucleus of any defined strength. The ratios of these frequencies are pure numbers in most cases, although for certain defined vibrations there is a small correction involving the ratio of mass of the electron and nucleus. We may search for vibrations, falling into groups with the prescribed ratios among individual members, in any spectrum that is known to emanate from matter of the simplest form—determined by the fact that no known element heavier than helium, for instance, is indicated as being present—and if such a spectrum is found which falls completely into such groups there is an a priori case for the conclusion that we have given a theory of the spectrum which is satisfactory, and of necessity settles many points of atomic structure.

The nebulæ and the solar corona have been generally believed to consist of the simplest forms of matter. They have always been invoked by speculators on the periodic table and its possible "early" elements, and with much reason. The spectrum of a nebula, for instance, contains only lines of hydrogen and helium, and others which cannot be produced in the laboratory after every possible mode of deriving them from likely elements has been tried. The spectrum of the corona, whilst rich in lines, contains nothing that can be produced in the laboratory. Naturally, in a search for the groups in specified numerical ratios, derived from precisely described atoms, we began with these spectra. The results were startling. The coronal spectrum consists entirely of lines—in number about thirty-six—which all fit precisely into the scheme of ratios for elementary atoms in which the nucleus has a charge $5e$ or $7e$, and five or seven electrons rotating round it, as the case

may be, in its normal state, and smaller or greater numbers in its charged states. The chemical identity of the atom must be regarded as determined by the charge of its nucleus—or its atomic number. The whole coronal spectrum can thus be linked up as the superposed spectra of two chemical substances, and represented by simple formulæ. It was found, moreover, that these formulæ would go further and predict the existence of new and unobserved spectrum lines. A notable instance was the coronium line $\lambda\,6374$ found by MM. Deslandres and Carrasco some time after the publication of the formula which predicted it, and similar predictions in the case of the spectra of planetary nebulæ have been verified. The corresponding substances in the nebulæ which are invoked as hypothetical entities are the same in kind as those for the solar corona, differing only in nuclear charge or atomic number. It is curious to note that the atomic numbers of the necessary hypothetical atoms for nebulæ are the even numbers 2, 4, 6, and for the corona they are odd numbers, 5, 7. The coronal spectrum appears to come in the main from these hypothetical atoms endowed with strong negative charges, for instance, the atom $7e$ with 9 revolving electrons. This points to an abundance of negative electrons in the corona, unattached to atoms and readily capable of attachment. There is much evidence, at the same time, that the atoms themselves are endowed with very high velocities, and may be a new form of α-particle.

To return to our main argument. What all these atoms share in common is the fact that their angular momenta are simple multiples of a constant unit. Armed with this generalisation, we can calculate the spectrum of any of these hypothetical elements—say one in the nebulæ—from that of another of different chemical nature—say one in the corona. I ventured to put forward the suggestion that this was the real basis of the quantum theory, and that the angular momenta of the electrons in all atoms were related in this simple way to a universal constant of nature, which, being an angular momentum, had the proper dimensions, and even the proper numerical value, as calculation showed, of Planck's unit.

Dr. Bohr, in the theory of series spectra which he subsequently put forward, adopted this generalisation. Prof. Jeans is to address you on the subject the fringe of which we are now touching, so that I will proceed no further, but turn aside to another aspect of importance to chemists. We have seen already that in certain spectrum lines calculated in the way outlined above, there will be a small discrepancy of wave-length due to the fact that the nucleus itself oscillates, as well as the electrons, in the types of vibration producing these lines. Its mass must therefore enter into the

question in these special cases, and it enters as a small term of order m/M, where m is the mass of the electron and M that of the nucleus. From the discrepancies, we can calculate M/m, which, with our practical knowledge of H/m, where H is the mass of the hydrogen atom, gives us M/H, the *atomic weight* of the hypothetical atom. Very concordant results are obtained from these calculations. The atomic weight of coronium, the name given to the hypothetical atom causing the most striking line λ 5303 in the coronal spectrum, is 4·0, suggesting that it may be a helium atom radiating in an unusual manner in an unusual environment; but the atomic weight of the other element there required is 2·0, which corresponds with no known terrestrial element. Again, in the nebulæ, the two most important atoms required give atomic weights 1·3, 3·0, again with no known terrestrial equivalent. Yet, nevertheless, MM. Buisson and Fabry, by their method of determining the mass of a radiating atom from the interference of its radiation, experimentally confirmed the value 3·0, and showed that the element for which our value is 1·3 had an atomic weight greater than, but not much greater than, that of hydrogen. It seems necessary to presume the existence, in circumstances which we perhaps are unable to produce at present in the laboratory—and maintain for a length of time—of such atoms which may not be chemical elements in the sense ordinarily understood by that term.

We have, in fact, two alternatives. Either the atoms in question have not an existence or have not been produced terrestrially, or we have not yet excited them in the laboratory in the appropriate manner to produce such spectra. The latter alternative seems more probable. There is reason to believe that the coronal spectrum at least consists of a somewhat scattered " negative band" spectrum, produced in the presence of an excess of electrons by a very mild form of excitation. However that may be, these spectra, although without doubt the first spectra to receive a strict theoretical basis which is satisfactory, are not *series* spectra as known to us, being in the nature of their relations very analogous to, and without doubt a special case of, band spectra. Series spectra themselves, as defined above, cannot, as we have seen, be ascribed to dynamical vibrations about an atomic condition of steady motion.

Before we proceed to series spectra, we should perhaps state the assumptions involved in the above work. They are, in effect, identical with the conclusions derived by Sir Ernest Rutherford on experimental grounds about six months after the publication of the first paper in which some of these results were obtained. In fact, they can all be included in the statement that the nucleus is at least as small as an electron, and that the law of force between

electric charges is *strictly*—to an extreme order of approximation—that of the inverse square. It is not necessary at this point to emphasise the very definite atomic structure which these results imply. The law of inverse square, the small nucleus, the existence of Planck's constant as a universal angular momentum, are simple examples of what can be deduced. The law of at least some negative spectra of atoms, previously unknown, is another corollary. Many of these deductions have been confirmed by the later experimental work, on quite other ground, of Rutherford and of his colleagues, and have to a large extent become part of the essential basis of Bohr's theory of spectra and its extraordinary consequences, recently worked out by Paschen and others, in regard to the fine structure of lines in the spectrum of hydrogen.

The spectra which we have just described are not series spectra in the ordinary sense of the term. They are in all essentials band spectra. Their production in the laboratory from known materials involves a new type of experiment—an experiment in which a gas of extreme tenuity must be excited by an electric force insufficient to ionise the gas and thus detach an electron, but sufficient to show a "dynamical vibration" spectrum after an exposure of many hours. No such form of excitation has yet been tried in any experimental production of spectra, but it is now being tried by Dr. Merton. It appears to be the only hope of producing some of these elusive astronomical spectra in the laboratory, and thus reaching one of the goals of the astronomical spectroscopist.

It is already clear that series spectra cannot be "dynamical vibration" spectra from the reasons cited above. What are they? The only suggestion which has met with any considerable success is that of Dr. Bohr. Proceeding from the point of view outlined above, he supposes, for instance, that an atom of hydrogen can have one electron rotating with an angular momentum which is any multiple of $h/2\pi$, where h is Planck's constant. He calculates the energy in any such state of rotation—a *stationary* state—and assumes that radiation is emitted in the passage between two such stationary states of amount equal to the loss of energy between the states, and also of amount hv, where, in accordance with Planck's law, v is the frequency of the emitted vibration. He thus deduces the hydrogen spectrum as containing the frequencies

$$ v = B\left(\frac{1}{m^2} - \frac{1}{n^2}\right), $$

where m and n are any integers and B is a universal constant dependent on Planck's constant, the calculated value of which approximates in a remarkable way to Rydberg's universal constant of spectra. The theory does, in fact, reproduce the hydrogen

spectrum, although, of course, that of Ritz, founded on the magneton, did the same, and is too frequently ignored. I wish at this point to make a remark which seems to me essential, and relates to a matter not previously dealt with effectively by theoretical physicists intent upon constructing models of a hydrogen atom which can give the Balmer series spectrum. This spectrum consists of about six lines in the laboratory. The actual spectrum of the hydrogen *atom* contains more than a thousand lines, the rest being the so-called "secondary spectrum." At least six theories of a hydrogen atom have now been given, leading to the Balmer series as its spectrum. But none gives any clue to the origin of the secondary spectrum of hydrogen, which is the real key to the problem of atomic structure, for it is known to be due in the main to the hydrogen *atom*, and not the molecule. I regard the disentanglement of this spectrum into its component bands and series as the most fundamental problem of modern spectroscopy. It is the great simplicity of the formula for the Balmer series which renders it so easy to construct physical theories to account for it. These theories are, nevertheless, unable to carry conviction if they do not provide for a much more extensive spectrum of the hydrogen atom, and no theory has yet even begun this task, which is one of great difficulty in the case of an atom believed to contain only one electron.

I have naturally confined my attention mainly to the more fundamental matters which relate to the simplest chemical atoms. Time is too short to enter into many other interesting points, such, for instance, as the fine structure of the hydrogen lines, which Dr. Merton and I have been elucidating recently. It is now known, for instance, that the Balmer series is a principal series, and not a diffuse series, as hitherto assumed. This result alone has an important bearing on the mechanism of production of this series from an assigned atom. If we were to discuss the spectra of mixed gases or of molecules, a host of problems remains to be solved, and can only be solved by co-operation of the physicist and chemist. To give only one instance, we may ask a question. In a mixture of calcium and barium molecules, with perhaps a temporary association CaBa, what relation would the spectrum of such a molecule have to those of the calcium and barium molecules? The whole question of the spectra of the temporary associations found in vacuum tubes, and analysed by Sir J. J. Thomson's method of "positive rays," remains for solution. All such work will bear on the problem of atomic structure, for an atom is not satisfactory unless it also forms molecules the spectra of which are deducible from that of the atom. No present model of a hydrogen atom appears as yet to have succeeded.

The Quantum Theory and New Theories of Atomic Structure.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON MAY 1ST, 1919.

By JAMES HOPWOOD JEANS.

THE problem of the structure of matter falls into two parts: first, the problem of determining the constituent parts of matter, and second, that of determining the laws according to which these constituent parts move and react with one another.

It has for some time been universally accepted that the fundamental constituents of matter are electrical in their nature, consisting of bodies of infinitesimal size carrying electric charges which are inseparable from them. Briefly speaking, matter is made up of positive and negative charges of electricity. The properties of the bodies carrying the negative charges are fairly well known. These bodies are the negative electrons; they all carry precisely the same charge and have precisely the same mass. They are independent of the chemical nature of the substance to which they belong, and so form standardised and interchangeable parts of all atoms. The same electron which at one instant forms part of an atom of hydrogen may at some future instant form part of an atom of iron; at another instant it may play the rôle of a "free" electron, its motion contributing to the carrying of an electric current through a mass of metal or of gas.

The properties of the positive charges, or "nuclei" as they are commonly called, are known with less certainty. I will try to discuss these properties in their logical order rather than in the chronological order of their discovery. Rutherford has proved that the α-rays emitted by radioactive substances are positively charged particles; he has shown that they all carry the same charge, and that this is equal, numerically, to twice the charge carried by a negative electron. If $-e$ is the charge carried by each negative electron, the α-particle carries a charge $+2e$. Thus an α-particle and two negative electrons would form a system carrying zero charge—an electrically neutral system. The system constituted in this way has been shown by Rutherford to be the normal helium atom. Thus the positive nucleus of the helium atom is simply the α-particle; its charge is $+2e$; its mass is, of

course, the mass of the helium atom minus twice the mass of a negative electron. Since the mass of the helium atom is about 7300 times that of a negative electron, we may say that the positive nucleus carries practically all the mass of the helium atom.

The size of the negative electron is well known. The variation of its mass with its velocity proves that the whole of its mass is electromagnetic, and this circumstance enables us to assign to it the definite radius 2×10^{-13} cm. The size of the helium atom is also known—from the kinetic theory of gases. Its radius is almost exactly 10^{-8} cm., or just about 50,000 times that of the negative electron.

We are led to wonder whether the positive nucleus carries most of the "size" of the atom as well as most of its mass. The answer is provided by experiments on the scattering of α-particles by matter. Imagine a jet of α-particles directed on to a thin sheet of matter. If the α-particles were of the size of helium atoms, it is clear that they would be obstructed at every point by the atoms of the matter, and would not emerge as a jet at all. It has, in point of fact, been found that the majority of the α-particles emerge with their paths only slightly deflected by their encounters with the atoms of the matter, whilst a few have their paths deflected through quite large angles. The inference which must be drawn is that not only are the α-particles excessively minute, but also that the parts of the atoms which are effective in deflecting the paths of the α-particles are themselves excessively minute. The actual amount of scattering observed agrees quantitatively with this conclusion, provided it is assumed that each atom contains only one positive nucleus, its size being infinitesimal compared with the size of an atom, and its charge being approximately proportional to the atomic weight of the matter.

Thus the normal atom is found to consist of a certain number, N, of negative electrons, each of charge $-e$, and a positive nucleus of extremely minute size and of charge Ne. For helium we have already seen that $N=2$, and the question immediately arises as to the value of N for other elements.

This problem has been solved by experiments on the X-ray spectra of the elements. Suppose the elements are arranged in order of their atomic weight, beginning with hydrogen, the lightest, leaving unoccupied gaps where the periodic law suggests that an element remains to be discovered, for example, between tungsten and osmium, and reversing the order of elements where this is demanded by the periodic law, so that, for instance, cobalt is placed before nickel and argon before potassium. The "atomic number" N of any element is that which represents its position in

this series.   Thus for hydrogen $N=1$, for helium $N=2$, for lithium $N=3$, for argon $N=18$, for potassium $N=19$, for silver $N=47$, and so on.   Then Moseley and others have proved—and I think most physicists are content to accept the proof as conclusive—that the number of negative electrons in the normal uncharged atom of any element is equal to the atomic number N of that element.   The charge on the positive nucleus of an atom of an element is accordingly Ne, where N is the atomic number of the element.

This settles, I think, in the opinion of most physicists, finally and incontrovertibly, the problem of determining the ingredients of the atom.   The uncharged hydrogen atom consists of a single negative electron of charge $-e$ and a positive nucleus of charge $+e$, the mass of which is something like 1840 times that of the negative electron.   The uncharged helium atom consists of two negative electrons and a nucleus of charge $2e$, and so on.

The problem of determining how these constituents are arranged and move inside the atom is still far from complete solution.   The material we have to work on consists almost entirely of the spectra of the elements; these provide a mass of data which admit of accurate measurement to five, or even six, significant figures. Knowing the structure of, say, the hydrogen atom, we could calculate its spectrum if we knew its laws of motion, just as Newton, conjecturally knowing the law of gravitation, could calculate what the orbit of a planet ought to be.

Suppose, for instance, that the positive nucleus and the negative electron, which form the normal hydrogen atom, moved according to the ordinary electrostatic law, by which the force varies as the inverse square of the distance.   The positive nucleus, being 1840 times more massive than the negative electron, would remain practically at rest, whilst the electron would describe an elliptical orbit about it.   The radiation which would be emitted by an electron describing such an orbit can readily be calculated.   There would be orbits of all possible sizes, and therefore of all possible periods, so that the emitted radiation would be of all possible frequencies—in other words, the spectrum would be continuous. Since the spectrum of the hydrogen atom consists of sharply defined lines, it is therefore at once clear that the motion in the hydrogen atom is not governed by the ordinary electrostatic laws.   Precisely similar reasoning shows that the electron cannot move under any continuous force from the positive nucleus.

Knowing the laws of motion, we could determine the spectrum. Unfortunately, the converse problem is not soluble; knowing the spectrum, we cannot deduce the laws of motion.   Some knowledge of a general kind can be obtained—in particular, the laws of motion

are necessarily discontinuous, for continuous laws of motion would lead to a continuous spectrum.

So far, we have considered the atomic spectrum. A somewhat similar situation presents itself when we turn to the consideration of the continuous spectrum of a solid. Except for irregularities arising from imperfect emission of the surface, all solid bodies give the same spectrum at the same temperature. The nature of this spectrum depends on the laws which govern the motion of the electrons by which the radiation is emitted. Different spectra would correspond with different laws of motion, and conversely. Again, if we knew the laws of motion, it would be possible to determine the spectrum.

If the motion of the electrons were governed by the classical laws of mechanics (Newton's laws), it can be shown that the spectrum would be of a very special type—there would be no wave-length of maximum energy, but the energy would increase indefinitely as the wave-length decreased. Thus the total spectral energy at any finite temperature would be infinite, all the energy running into the waves of shortest wave-length. It is therefore clear that the motion of electrons is not governed by the classical laws of mechanics.

In 1901 Planck, starting from a system of laws which differed entirely from the classical laws, and in particular involved the idea of discontinuous motion, arrived at a spectral formula which has since been found to agree extremely well, probably perfectly, with the observed spectrum of a solid. Although Planck's spectral formula, regarded as an expression of a fact of nature, has since gained universal acceptance, his method of deducing it has been widely objected to, mainly on account of his assumption of discontinuous motion. In 1910 I was able to show that Planck's formula could not possibly be arrived at except from a system of laws which involved discontinuities of some kind, and, further, I found that the nature of these discontinuities must necessarily be substantially of the type already assumed by Planck. Almost identical conclusions were enunciated by Poincaré about a year later, together with important additions.

Thus from a study of the continuous spectrum of a solid we conclude that the motion of the radiation-emitting electrons must be of a discontinuous nature. It is, unfortunately, not possible to specify the nature of these discontinuities completely, but a good deal is known. When the electron is executing isochronous vibrations, the total energy of the vibration (potential plus kinetic) must fall into "quanta." The energy may be equal to one quantum, two quanta, etc., but cannot involve fractions of the quantum. Thus

when the energy changes, there must be an instantaneous absorption or emission of a whole quantum of energy. In general, however, when the energy of a vibration changes, the frequency also changes. Now the "quantum" of energy is not the same for all vibrations; it depends on the frequency of the vibration. If v is the frequency, the quantum is hv, where h is a universal constant of nature—Planck's "Wirkungsquantum." Thus if an electron jumps from a vibration in which it has n_1 quanta, its frequency being v_1, to a vibration in which it has n_2 quanta, its frequency being v_2, it must instantaneously emit an amount of energy $h(n_1v_1 - n_2v_2)$.

Evidence as to what happens to the energy thus suddenly emitted is provided by the photoelectric phenomenon. To ionise an atom of any substance requires an amount of energy, Q, which depends on the nature of the atom. Now the atoms of any substance can be ionised by light, but only by light the frequency of which is above a critical value v_0, which again depends on the nature of the atom. This frequency v_0 is related to the energy Q required for ionisation by the relation $Q = hv_0$ (approximately at least). Thus it looks as though light of frequency v travelled through the ether tied up in some way in bundles of amount hv—in fact, in quanta. This is Einstein's hypothesis of light-quanta; no doubt it does not express the whole truth, but it must be somewhere near to the truth.

Accepting this hypothesis provisionally, the amount of energy, $h(n_1v_1 - n_2v_2)$, which we imagined to be set free from one atom, will wander through space as a single quantum; in order that it may satisfy the quantum relation (energy $= hv$), its frequency must be $n_1v_1 - n_2v_2$.

On these foundations, Bohr has, with extraordinary skill and acumen, developed his theory of line-spectra. The frequency v_1 of the original vibration having n_1 quanta must depend on n_1, and similarly v_2 must depend on n_2. Thus the frequency of the emitted vibration will be expressible mathematically in a formula of the type

$$f_1(n_1) - f_2(n_2),$$

and on giving all possible values to n_1 and n_2, we ought to obtain the whole line-spectrum of the element.

The case of the hydrogen atom is particularly simple. To a first approximation we may consider the massive positive charge as being at rest, and the formula is found to be

$$N\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$

This gives exactly the hydrogen spectrum (Balmer's series being given by $n_1 = 2$, Lyman's series by $n_1 = 1$, etc.) provided N is equal to Rydberg's constant. Now the theoretical value of N depends only on universal constants of nature. The value of each of these is known to about 1 part in 200, and on inserting these values, the theoretical value of N is found to be equal to Rydberg's constant to about 1 part in 200. There is thus the most brilliant agreement, both quantitatively and qualitatively, between the observed spectrum of hydrogen and the theoretical spectrum predicted by Bohr's theory.

The assumption that the massive positive nucleus stands at rest is only approximately true; actually it will oscillate round the centre of gravity of itself and the negative electron, and this will introduce a correction of the order of M/m, the ratio of the mass of the nucleus to that of the electron. By comparing the theoretical correction with spectroscopic observations, Fowler has deduced for M/m the value 1835, a value which agrees exceedingly well with other determinations of M and m.

Still one other correction of a most fascinating kind must be mentioned. Bohr's theory takes its simplest form when the electron orbits are assumed to be circular; the simple spectral laws are exact for circular orbits. Consistently with the quantum dynamics, however, the electron can also describe a series of elliptic orbits. This possibility gives rise to a new series of frequencies which differ only from those of circular orbits by quantities of the order of $(v/V)^2$, where V is the velocity of light and v that of the electron in its orbit. The theory of relativity makes it possible to calculate the corrections to the frequencies introduced by the ellipticities of the orbits. Sommerfeld has carried the calculation through, and believes that the whole series of frequencies exactly account for the fine structure of the spectral lines. The agreement, so far, is limited to the single line H_a; for this, it is perfect both qualitatively and quantitatively, and I venture to predict that a similar explanation will soon be found of the fine structure of other lines.

This is as far as we can go with any confidence. It seems to me that experimental evidence and abstract reasoning combined practically limit us to one view of the structure and mechanism of the simpler atoms, and this view is confirmed by a large amount of exact spectroscopic evidence. The structure is that of the so-called Rutherford atom; the simpler atoms (hydrogen and helium at least) consist of an extremely minute central nucleus with one or more negative electrons revolving round. The mechanism is

that of Bohr's theory, and is based upon, and governed by, the quantum dynamics.

We cannot, I think, claim to know anything with certainty as to the ultimate structure of the more complex atoms, especially those of radioactive substances, and our definite knowledge of atomic mechanism is practically limited to the few cases in which the atom contains only two constituents—the hydrogen atom, the positively charged helium atom, and possibly also the doubly-charged lithium atom. The "problem of three bodies" has not yet been solved in quantum dynamics any more than in gravitational theory. This is scarcely surprising in view of the fact that the whole quantum theory is wholly a creation of the present century.

We cannot speak with any confidence as to the mechanism of complete molecules other than the monatomic helium molecule; for even the simplest complete molecule, the hydrogen molecule, consists of four constituent parts. If progress continues at its present rate, however, there is every reason for hoping that within a few years the whole scheme of quantum-mechanics will have been unravelled. The problems of valency, stereochemistry, the periodic law, the stability of chemical compounds, their optical and colour properties, and a host of other chemical problems, will then become the province of the mathematician. In spite of the rapidly progressing fusion of all branches of science, the chemist and the mathematician have up to the present remained almost independent. It seems possible that in the near future the chemist will scarcely think of making progress except with the help of the mathematician. In spite of its history of extraordinary triumphs, chemistry is to-day as much an empirical science as electricity was before the time of Maxwell. If once chemistry becomes a mathematical science, it may progress at a rate at present undreamed of.

LXXII.—*Interaction of Mercuric and Cupric Chlorides Respectively and the Mercaptans and Potential Mercaptans.*

By PRAFULLA CHANDRA RÂY.

SOME four years ago, the author ventured to put forth the view that the compounds which mercuric, platinic, and cupric chlorides, respectively, yield with thiocarbamide and thioacetamide, etc., are of the same nature as those obtained by the interaction of these

haloids and real mercaptans, that is, they are chloromercaptides (P., 1914, **30**, 304), and it seemed desirable to undertake a systematic study of the behaviour of mercuric, cupric, and platinic chlorides towards some of the typical mono- and di-mercaptans, namely, ethyl and ethylene mercaptans (dithioethylene glycol) and 2-thiol-5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole.

Ethyl mercaptan yields under normal conditions chloroplatinum mercaptide, $(EtS)_2PtCl$, and under exceptional conditions platinous mercaptide, $(EtS)_2Pt$. Dithioethylene glycol also yields a chloro-mercaptide of the formula $C_2H_4{<}{}^S_S{>}PtCl\cdot S\cdot C_2H_4\cdot SH$.   In the formation of this remarkable compound, two molecules of dithio-ethylene glycol simultaneously take part in the reaction; one atom of chlorine of the platinic chloride remains, however, intact.

The potassium salt of 2-thiol-5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole has been found to be equally reactive towards platinic chloride, and it readily yields mercaptides in which platinum functions both as a triad and a dyad element, as in the case of the simple ethyl mercaptan.

The valency of platinum calls for a few remarks. The salts of the type MX_3 are scarcely represented among the platinum compounds. In the formula $(EtS)_2PtCl$, no doubt platinum may be made to appear as quadrivalent by doubling it. Platinum has its proper place in the eighth or transitional group in the periodic system, which also includes iron and iridium. Now, the chlorides of these metals are represented by the simple formula MCl_3, and not by M_2Cl_6. Moreover, platinum, with the high atomic weight of 194, will scarcely permit of the coalescence of two atoms into the complex :Pt·Pt:. Salts containing two atoms of platinum in the molecule have no doubt been described, but they are of a very complex character (Cossa, *Ber.*, 1890, **23**, 2503; Cleve, *Bull. Soc. chim.*, 1872, **17**, 289).

The product of the reaction of mercuric chloride with thiocarb-amide has been assigned the formula $HgCl_2,CSN_2H_4$ (Rosenheim and Meyer, *Zeitsch. anorg. Chem.*, 1903, **34**, 62; 1906, **49**, 13). In other words, it has been regarded as a mere additive or mole-cular compound. From considerations based on analogy, the author suggested that it should be formulated as

$$[NH_2\cdot C(:NH)\cdot S\cdot HgCl]HCl,$$
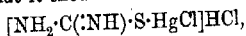
that is, that it is the product of the reaction of mercuric chloride on ψ-thiocarbamide. The hydrogen chloride which is formed is not liberated in the free state, but is simply fixed by the basic complex. It is well known that formamidine disulphide exists as a salt of a diacidic base, because of the presence of two amino- and

imino-groups. Convincing proof has recently been obtained in support of the above formula. The compound in question has been found to be sufficiently soluble in water to admit of conductivity measurements. If it were an additive one, it would dissociate into its components on dissolution. Now, thiocarbamide is practically a non-electrolyte, and mercuric chloride is very feebly ionised in solution (compare Rây and Dhar, T., 1913, **103**, 8).

The aqueous solution, however, shows an enormous increase in the dissociation, which is of the same order as that of ammonium chloride, proving that the salt is the hydrochloride of a base.

Thiocarbamide may be expected to behave in like manner towards platinic chloride and yield a compound of the same type, thus: $2CS(NH_2)_2 \xrightarrow{PtCl_4} [(NH_2 \cdot C(\vdots NH) \cdot S)_2 PtCl_2]HCl$. Both Reynolds and Prätorius-Seidler (compare Rathke, *Ber.*, 1884, **17**, 307), however, regard the compound as an additive one of thiocarbamide with platinous chloride, and assign to it the formula $(CSN_2H_4)_2 PtCl_2, HCl$ or $(CSN_2H_4)_2 PtHCl_3$. That this view is erroneous is evident from another consideration. The platinic chloride on being reduced to the platinous state would set free chlorine, which would in turn act on a portion of the thiocarbamide, and formamidine disulphide hydrochloride would be simultaneously formed; * the derivative in question is, however, free from it.

Cupric chloride is analogous in its behaviour towards thiocarbamide, $CS(NH_2)_2 \xrightarrow{CuCl_2} NH_2 \cdot C(\vdots NH) \cdot S \cdot CuCl$. In this case, however, the hydrogen chloride is liberated in the free state and can be detected in the filtrate. This is what might have been expected. The chlorides of mercury, platinum, and cobalt are capable of forming complex compounds with ammonia, amines, and aminogroups, which, on account of their basic character, can fix a molecule of hydrogen chloride, whilst copper, being a more positive metal, does not possess this property.

The view taken above offers also a ready interpretation of the reaction between platinic chloride and thioacetamide, first studied by Kurnakov (*J. Russ. Phys. Chem. Soc.*, 1893, **25**, 613), who formulates the compound as $PtCl_2, 4C_2H_5NS, PtCl_4$, that is, as an additive one of four molecules of thioacetamide with one of platinous chloride and another of platinic chloride. This formula, when halved, stands as $PtCl_3, 2C_2H_5NS, HCl$, and is in reality $[(CH_3 \cdot C(\vdots NH) \cdot S)_2 PtCl_2]HCl$, the platinic chloride functioning

* It has been actually found that sulphuryl dichloride, which acts as a mild chlorinating agent, behaves exactly like iodine towards thiocarbamide and yields the hydrochloride of the base.

exactly like mercuric chloride. Thioacetamide here also simply undergoes tautomeric change. One strong argument in favour of the suggested constitution is afforded by the fact that if platinic chloride were actually to be reduced to the platinous form, the available atoms of chlorine would act on two other molecules of thioacetamide. It has already been shown that iodine completely decomposes thioacetamide, the whole of the sulphur being precipitated (T., 1916, **109**, 698). The product in question when treated with carbon disulphide, however, did not yield any sulphur. The corresponding cupric chloride derivative has been found to conform to the formula $CH_3 \cdot C(:NH) \cdot S \cdot CuCl$; it is, in fact, a chloromercaptide.

The reaction between platinic chloride and thiosemicarbazide is of special interest. The compound obtained has the formula $C_3H_4N_6Cl_2S_3Pt$. Here also a tautomeric change of the thio-compound evidently takes place under the influence of the haloid, resulting in the formation of a cyclic compound with the elimination of a molecule of ammonia, thus:

$$NH_2 \cdot CS \cdot NH \cdot NH_2 \longrightarrow NH:C(SH) \cdot NH \cdot NH_2 \longrightarrow$$
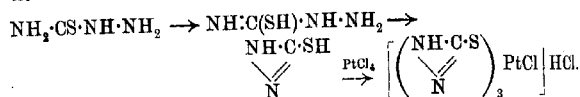
The mercaptan now acts on platinic chloride in the usual manner, the product being a chloromercaptide. Of the three molecules of hydrogen chloride generated, one is fixed by the complex substance because of its basic character, due to the presence of several imino-residues.

<div align="center">EXPERIMENTAL.</div>

<div align="center">*Mercaptans and Metallic Haloids.*</div>

Ethyl Mercaptan and Platinic Chloride.—Hofmann and Rabe (*Zeitsch. anorg. Chem.*, 1897, **14**, 294) state that if to chloroplatinic acid is added ethyl mercaptan in alcoholic solution, at first an orange-yellow platinic mercaptide, $(EtS)_4Pt$, is formed which, when heated to $100°$ in a vacuum, readily yields platinous mercaptide. It has been found, however, that by the interaction of platinic chloride and ethyl mercaptan, chloroplatinum mercaptide, $(EtS)_2PtCl$, is almost invariably formed, and that it is only under exceptional conditions that platinous mercaptide, $(EtS)_2Pt$, can be obtained. The method is therefore given here somewhat in detail. To a concentrated alcoholic solution of chloroplatinic acid is added a very dilute alcoholic solution of ethyl mercaptan from time to time with vigorous shaking; for the first

few moments, only a deep orange coloration is noticed, but shortly after an orange-yellow precipitate begins to appear. Care should be taken that the platinic chloride is always in sufficient excess. If the conditions of reaction are reversed, that is, if a dilute solution of platinic chloride is added in small quantities at a time to an excess of a concentrated alcoholic solution of ethyl mercaptan with vigorous shaking, for a few minutes the solution remains clear, after which a yellow salt begins to separate, which is very nearly pure platinous mercaptide.

Chloroplatinum mercaptide:

I. 0·050 gave 0·0276 Pt, 0·022 AgCl, and 0·065 $BaSO_4$.*
   Pt=55·2; Cl=11·33; S=17·85.
II. 0·0502 gave 0·0283 Pt and 0·0675 $BaSO_4$. Pt=56·37;
   S=18·47.
III. 0·0226 gave 0·0126 Pt. Pt=55·75.
IV. 0·0191 gave 0·0081 AgCl and 0·0242 $BaSO_4$. Cl=10·51;
   S=17·44.
$C_4H_{10}ClS_2Pt$ requires Pt=55·02; Cl=10·09; S=18·19 per cent.

Platinous mercaptide:

0·1317 gave 0·0814 Pt, 0·012 AgCl, and 0·1985 $BaSO_4$.
   Pt=61·81; Cl=2·25; S=20·71.
   $C_4H_{10}S_2Pt$ requires Pt=61·43; S=20·24 per cent.
Contamination with distinct traces of the previous compound, which is invariably formed, accounts for the presence of chlorine.
2-Thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole,

$$\begin{array}{c} NPh\cdot N \\ | \quad\quad >C\cdot SH. \\ CS \text{---} S \end{array}$$
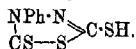
and Platinic Chloride.—To a concentrated aqueous solution of the potassium salt was added, with stirring, a dilute solution of chloroplatinic acid in a thin stream. A yellow precipitate was obtained which, on drying, became orange. Here also, as in the case of ethyl mercaptan, the platinum atom functions as tervalent and bivalent:

0·080 gave 0·0213 Pt and 0·1805 $BaSO_4$. Pt=26·63; S=31·00.
A second preparation gave Pt=25·32.
   $(C_3H_5N_2S_3)_3Pt$ requires Pt=22·33; S=33·14.
   $(C_3H_5N_2S_3)_2Pt$ requires Pt=30·12; S=29·18.
Mean: Pt=26·23; S=31·16 per cent.
It will thus be seen that here also a compound containing quadri-

* The estimation throughout was effected by fusion with sodium nitrate and sodium carbonate.

valent platinum is never formed, but a mixture of almost equal proportions of the compounds containing tervalent and bivalent platinum.

In the above reactions, the free hydrogen chloride of chloroplatinic acid, acting on a portion of the potassium mercaptide, liberates the corresponding mercaptan, which is insoluble in water, and the available chlorine atoms of the quadrivalent platinum chloride also acting on the potassium mercaptide give rise to the disulphide, which is equally insoluble. The dried precipitate was therefore exhausted first with alcohol and afterwards with benzene in order to extract impurities. The colour of the compound changed from yellow to orange under this treatment.

Dimercaptans and Metallic Haloids.

Dithioethylene Glycol and Platinic Chloride.—A dilute alcoholic solution of platinic chloride was gradually added, with vigorous stirring, to a concentrated alcoholic solution of dithioethylene glycol. A yellowish-brown precipitate was obtained, which was washed with alcohol and dried in a vacuum. It conforms to the formula $C_2H_4\!\!<^S_S\!\!>PtCl\cdot S\cdot C_2H_4\cdot SH$:

0·0788 gave 0·0373 Pt, 0·032 AgCl, and 0·1608 BaSO$_4$. Pt$=47·34$; Cl$=10·05$; S$=28·03$.

$C_4H_9ClS_3Pt$ requires Pt$=46·96$; Cl$=8·58$; S$=30·93$ per cent.

There is reason to conclude that a simpler mercaptide of the formula $C_2H_4\!\!<^S_S\!\!>PtCl_2$ (Pt$=54·39$; Cl$=19·88$; S$=17·91$) is simultaneously formed in small quantities; the higher results for platinum and chlorine and the lower result for sulphur are thus accounted for. Attempts to obtain the chloromercaptide in a purer form proved unsuccessful.

Potential Mercaptans and Metallic Haloids.

Thiocarbamide and Mercuric Chloride.—The components interacted both in alcoholic and in aqueous solution; a copious white precipitate was obtained, which was washed with alcohol and dried in a vacuum. The filtrate was neutral. (Found: C$=3·82$; H$=1·63$; N$=8·14$; Cl$=20·45$; S$=10·03$; Hg$=56·62$. $CH_4N_2Cl_2SHg$ requires C$=3·46$; H$=1·18$; N$=8·07$; Cl$=20·46$; S$=9·22$; Hg$=57·64$ per cent.)

Conductivity Measurement.

$V.$	$T.$	$\mu.$
256	21·5	98·96

There were evidently two ions in solution, and the dissociation is of the order of that of ammonium chloride.

Thiocarbamide and Platinic Chloride.—An acetone solution of thiocarbamide was cautiously added, with constant stirring, to platinic chloride solution. An orange-yellow precipitate was obtained, which was washed with alcohol and dried in a vacuum:

I. 0·0838 gave 0·0365 Pt, 0·0910 $BaSO_4$, and 0·0804 AgCl.
   Pt = 43·56; S = 14·91; Cl = 23·74:
   0·0582 gave 6·6 c.c. N_2 at 33° and 760 mm.   N = 12·39.

II. 0·0496 gave 0·0540 $BaSO_4$ and 0·0482 AgCl.   S = 14·95;
   Cl = 24·03.

$C_2H_7N_4Cl_3S_2Pt$ requires Pt = 43·01; S = 14·17; Cl = 23·57;
   N = 12·40 per cent.

Thiocarbamide and Cupric Chloride.—To an alcoholic solution of cupric chloride was added, with constant stirring, an alcoholic solution of the carbamide. The granular precipitate when dried in a vacuum was white with a faintly blue tint:

0·0608 gave 0·0275 CuO.   Cu = 36·09.
0·0443 ,,   6·2 c.c. N_2 at 31° and 760 mm.   N = 15·41.
0·0588 ,,   0·0483 AgCl and 0·0780 $BaSO_4$.   Cl = 20·31;
   S = 18·22.
CH_3N_2ClSCu requires Cu = 36·38; N = 16·12; Cl = 20·44; S = 18·43
   per cent.

Thioacetamide and Platinic Chloride.—Thioacetamide in alcoholic solution was added, with stirring, to platinic chloride solution, and the brownish-yellow precipitate was treated as before:

I. 0·0852 gave 0·0360 Pt; 0·0782 AgCl.   Pt = 42·26;
   Cl = 22·79.

II. 0·0334 gave 0·0144 Pt.   Pt = 43·11.
   0·0813 ,,   5·2 c.c. N_2 at 32° and 760 mm.   N = 7·01.

III. 0·1457 gave 0·0630 Pt, 0·1697 $BaSO_4$, and 0·1313 AgCl.
   Pt = 43·83; S = 15·99; Cl = 22·29.

$C_4H_9N_2Cl_3S_2Pt$ requires Pt = 43·20; S = 14·23; Cl = 23·68;
   N = 6·23 per cent.

Thioacetamide and Cupric Chloride.—The method of preparation was exactly the same as in the preceding case, the salt being almost white. The alcoholic filtrate, when distilled off, was found to contain free hydrogen chloride:

I. 0.0555 gave 0.0250 CuO. Cu $= 35.95$.

$\quad$ 0.0595 ,, 4.6 c.c. N_2 at $29.5°$ and 760 mm. N $= 8.57$.

II. 0.2818 ,, 0.1261 CuO, 0.42 BaSO$_4$, and 0.2250 AgCl.
$\quad$ Cu $= 35.78$; S $= 20.44$; Cl $= 19.75$.

$C_2H_4NClSCu$ requires Cu $= 36.59$; S $= 18.53$; Cl $= 20.55$; N $= 8.11$
$\quad$ per cent.

Thiosemicarbazide and Platinic Chloride.—A dilute solution of platinic chloride was added to a concentrated aqueous solution[*] of thiosemicarbazide. In the course of half an hour, a granular precipitate began to be deposited, and the solution was allowed to remain overnight. The granules, when collected and dried, were yellowish-white:

$\quad$ 0.2864 gave 0.1171 Pt, 0.1719 AgCl, and 0.387 BaSO$_4$.
$\quad$ $\quad$ Pt $= 40.89$; Cl $= 14.85$; S $= 18.56$.

$\quad$ 0.0381 gave 6.2 c.c. N_2 at $30°$ and 760 mm. N $= 17.97$.

$\quad$ $C_3H_4N_6Cl_2S_3Pt$ requires Pt $= 40.04$; Cl $= 14.63$; S $= 19.78$;
$\quad$ $\quad$ $\quad$ $\quad$ N $= 17.31$ per cent.

Summary and Conclusion.

(1) Whilst mercuric chloride reacts with a mercaptan to yield a chloromercaptide, thus, $R{\cdot}SH + HgCl_2 = R{\cdot}S{\cdot}HgCl + HCl$, cupric and platinic chlorides generally give mercaptides or mercaptides with only a slight admixture of chloromercaptides.

(2) Platinum in relation to monomercaptanic radicles functions either as tervalent or bivalent.

(3) The above chlorides bring about tautomeric changes in thio-carbamide and thioacetamide. Thiosemicarbazide with platinic chloride also undergoes similar transformation and yields a cyclic degradation product, $\underset{N}{\overset{NH\cdot C\cdot SH}{\diagdown\!\!\diagup}}$.

(4) The chloromercaptides of the potential mercaptans, inasmuch as they contain one or more imino-groups, are capable of fixing a molecule of hydrogen chloride, and in fact are hydrochlorides of complex bases.

[*] Thiosemicarbazide is almost insoluble in cold alcohol, ether, or acetone.

THE Council has ordered the following letter and report to be printed in the Journal of the Society:

> WHINFIELD,
> SALCOMBE,
> S. DEVON.
> *June 23rd,* 1919.

GENTLEMEN,

I have the honour to submit a Report from the International Committee on Atomic Weights relative to such accounts of experimental work on atomic weights as have been published since their last regular Report of 1916, together with a table which it is suggested should be adopted in place of that now in use.

It will be seen that the Report deals with the atomic weights of hydrogen, carbon, bromine, boron, fluorine, lead, gallium, zirconium, tin, tellurium, yttrium, samarium, dysprosium, erbium, thorium, uranium, helium, and argon.

In the accompanying table for 1920, changes from the values hitherto adopted are recommended for argon, boron, gallium, thorium, and yttrium, and the atomic weight of nitrogen should be changed from 14·01 to the more precise value 14·008, which is probably accurate to within 1 in the third decimal place.

> I am, Gentlemen,
> Your obedient Servant,
> T. E. THORPE.

The Hon. Secretaries,
The Chemical Society,
London.

Report of the International Committee on Atomic Weights for 1919–1920.

The last regular report of this committee, apart from an annual recommendation to continue the use of the table of atomic weights then presented, was published in 1916. The interruption in the series of reports was, of course, due to the world war, which created difficulties of a serious kind among all international organisations. Co-operation with Germany became impossible, partly because of the difficulties of correspondence and partly because of the personal hostilities created by the conduct of the war. There was also an inevitable slackening of scientific activities, and this was well shown by the unusually small number of new researches

in the field of atomic weights. Now that peace is in sight, it seems wise to resume the preparation of these reports, even though they may not be for some time yet quite so truly international as heretofore. The determinations published since the preparation of our last report may now be summarised, as follows:

Hydrogen.—A very thorough investigation by Burt and Edgar* (*Phil. Trans.*, 1916, [*A*], **216**, 393) on the volumetric composition of water has given the volume ratios of H to O as 2·00288:1. From this value, taking the normal litre weights of oxygen and hydrogen as 1·42900 and 0·089873 gram respectively, the atomic weight of hydrogen becomes 1·00772, or, rounded off, 1·0077. Guye (*J. Chim. Phys.*, 1917, **15**, 208), from a discussion of Burt and Edgar's data, accepts this value, as lying between the two extremes of 1·00767 and 1·00773. If, however, instead of trusting to the densities of the gases and their physical constants exclusively we take into account the admirable researches of Morley, Noyes, and others upon the synthesis and analysis of water,† the most probable general mean for the atomic weight of hydrogen becomes 1·0078, which differs from the volumetric value by only 1/10,000. That is, the two distinct lines of attack upon the problem agree within the limits of actual uncertainty. For ordinary purposes, the approximate value 1·008 is close enough. It must be remembered that the tables prepared by this committee are for the use, not so much of specialists, as of working chemists in general, and too much refinement will only lead to confusion. No determinations of these or any other constants can be absolute and final. All are subject to errors which may be reduced nearly, but not quite, to insignificance, but never eliminated entirely. For example, in the determination of atomic weights from gaseous densities, it is not possible to guarantee the *absolute* purity of the gases or to avoid errors in weighing, in reductions to a vacuum, or in the values given to the physical constants that are used in the final computations. Some of these errors may be so small as to be negligible, and in the aggregate they may tend either to reinforce or to compensate one another, but their extreme magnitude can be estimated with some approach to accuracy and expressed by means of the usual ± sign. At present, an accuracy to within 1/10,000 is the best we can expect to obtain.‡

* This research was noted in the previous report for 1917. Its review by Guye renders its repetition desirable here.

† Computation by F. W. C.

‡ For an elaborate discussion of sources of error in atomic weight determinations, see Guye and his colleagues (MM. Germann, Moles, and Renard) in *J. Chim. Phys.*, 1916, **14**, 25, 195, 204 ; 1917, **15**, 60, 360, 405 ; 1918, 16, 46.

Carbon—Two investigations on the atomic weight of carbon were reported from the Geneva laboratory in 1918. First, Stahrfoss (*J. Chim. Phys.*, 1918, **16**, 175) determined the density of acetylene, ethane, and ethylene. Acetylene proved to be unsatisfactory, because of its tendency to polymerise. From ethane he obtained the value $C = 12\cdot006$, and from ethylene $C = 12\cdot004$. On account of some uncertainties in the reductions, he prefers, provisionally, the value $C = 12\cdot00$.

Secondly, Batuecas (*J. Chim. Phys.*, 1918, **16**, 322) determined the density of ethane, and reduced his observations by three methods, giving $C = 12\cdot005$, $11\cdot999$, and $11\cdot996$. The last two, being concordant, he regards as preferable, and their mean, $C = 11\cdot998$, he adopts. It will be remembered that Richards and Hoover, by purely chemical methods, found $C = 12\cdot005$, and a later combination of all determinations published before 1918 gave the chairman of the committee the mean value $C = 12\cdot0025$. For ordinary purposes, the rounded-off value $C = 12\cdot00$ may be used, and is so given in the table.

Bromine.—Three sets of determinations of the molecular weight of hydrobromic acid have been made in Guye's laboratory at Geneva by Moles (*J. Chim. Phys.*, 1916, **14**, 389. See review by Guye in the same number, p. 361), Reiman (*J. Chim. Phys.*, 1917, **15**, 293), and Murray (*J. Chim. Phys.*, 1917, **15**, 334. Reiman and Murray assume $H = 1\cdot008$; Moles prefers $1\cdot0076$). The acid used was prepared by several distinct methods, and all gave concordant results, which may be summarised as follows, when $H = 1\cdot0078$:

	Mol. wt. HBr.	At. wt. Br.
Moles	80·9332	79·9254
Reiman	80·932	79·9242
Murray	80·930	79·9222

These values are wonderfully concordant, and the variations are far within the allowable limits of experimental error. In a recent combination, by the chairman of this committee, of all the available data relative to the atomic weight of bromine, the value found was $Br = 79\cdot9228$, in complete harmony with the Geneva determinations. For ordinary purposes, the rounded-off figure 79·92 is enough.

Boron and Fluorine.—In a very original investigation, Smith and Van Haagen (*Carnegie Inst. Washington, Publ.* No 267, 1918) have simultaneously redetermined the atomic weights of boron and fluorine. Their starting point was anhydrous borax, $Na_2B_4O_7$, and their chief difficulty was in insuring the complete dehydration of that compound. The salt was then converted, in a series of

K K*

successive experiments, into sodium sulphate, carbonate, nitrate, chloride, and fluoride, which gave eight independent values for boron ranging from $B = 10\cdot896$ to $10\cdot905$; in mean, $10\cdot900$. This value was computed with $Na = 22\cdot997$, $Cl = 35\cdot457$, $S = 32\cdot064$, $N = 14\cdot010$, and $C = 12\cdot005$. The authors finally discuss all previous determinations, and show wherein they were affected by errors. The new value, $10\cdot900$, should be adopted as the most probable.

In this research, sodium fluoride was compared, not only with borax, but also with the sulphate, and the eight values found ranged from $F = 19\cdot002$ to $19\cdot008$; in mean, $19\cdot005$. The rounded-off value, $F = 19$, may be retained for all practical purposes.

Lead.—Œchsner de Coninck and Gérard (*Compt. rend.*, 1916, **163**, 514) have attempted to determine the atomic weight of lead by calcination of the nitrate, and find $Pb = 206\cdot98$, when $N_2O_5 = 108$. This determination is evidently of no present value. With this exception, the other recent researches relative to this constant have referred to isotopic lead, and the normal element is considered only in comparison with it. Richards and Wadsworth (*J. Amer. Chem. Soc.*, 1916, **38**, 2613), for instance, find for normal lead $Pb = 207\cdot183$, and Richards and Hall (*J. Amer. Chem. Soc.*, 1917, **39**, 537) give $Pb = 207\cdot187$, values slightly lower than the accepted $207\cdot20$ as determined by Baxter and Grover. Similar determinations by A. L. Davis (*J. Physical Chem.*, 1918, **22**, 631) gave discordant results. As for isotopic lead, its atomic weight is so variable as to show that it is nearly, if not always, a mixture of isotopes, and not a constant which can as yet be placed in the table. The values found have very great significance, but they are far from final.*

Gallium.—By the analysis of carefully purified gallium chloride, Richards, Craig, and Sameshima (*Proc. Nat. Acad. Sci.*, 1918, **4**, 387) find $Ga = 70\cdot09$ and $70\cdot11$. These determinations, however, are only preliminary, but they justify the provisional adoption of the value $70\cdot10$. The original values given by the determinations of Lecoq de Boisbaudran vary from $69\cdot70$ to $70\cdot12$, the last one being very near the new value.

Zirconium.—From the ratios between zirconium chloride and silver, Venable and Bell (*J. Amer. Chem. Soc.*, 1917, **39**, 1598) find $Zr = 91\cdot76$. Although this determination is regarded as preliminary, the authors, by pointing out sources of error in all previous values, believe the new one to be the most probable. It

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* For discussions regarding the atomic weight of isotopic lead, see the Presidential address of Richards before the American Association for the Advancement of Science in December, 1918. Also F. W. Clarke, *Proc. Nat. Acad. Sci.*, 1918, **4**, 181.

seems best, however, to await the complete investigation before changing the value heretofore accepted.

Tin.—Baxter and Starkweather (*Proc. Nat. Acad. Sci.*, 1916, **2**, 718), by electrolyses of stannic chloride, find $Sn = 118.703$ when $Cl = 35.457$. This is in complete agreement with Briscoe's determination, $Sn = 118.698$. The value 118.70 has already been adopted by the committee.

Tellurium.—Staehler and Tesch (*Zeitsch. anorg. Chem.*, 1916, **98**, 1), from careful syntheses of tellurium dioxide, find $Te = 127.51$, which is confirmatory of the accepted value, 127.5.

Yttrium.—Hopkins and Balke (*J. Amer. Chem. Soc.*, 1916, **38**, 2332), by conversion of Yt_2O_3 into Yt_2Cl_3, find $Yt = 88.9$. The ordinary sulphate method is shown to be inaccurate. In a later investigation, Kremers and Hopkins (*J. Amer. Chem. Soc.*, 1919, **41**, 718) determined the ratio between yttrium chloride and silver, and found $Yt = 89.33$. Since this method is the most trustworthy, the value given by it should be adopted. The other sulphate determinations are questionable.

Samarium.—The atomic weight of samarium has been determined by Stewart and James (*J. Amer. Chem. Soc.*, 1917, **39**, 2605) from the ratio between the chloride and silver. The value found is 150.44, which is essentially that given in the table. No change is needed.

Dysprosium.—Engle and Balke (*J. Amer. Chem. Soc.*, 1917, **39**, 57), by conversion of the oxide into the chloride, found $Dy = 164.228$. Later, by the same method, Kremers, Hopkins, and Engle (*J. Amer. Chem. Soc.*, 1918, **40**, 598) found $Dy = 163.83$. This discordance, like that already shown for yttrium, led the last-named chemists to determine the ratio between dysprosium chloride and silver, which gave 162.52. The earlier method is discredited, and the last value, rounded to 162.5, seems to be the one best entitled to acceptance.

Erbium.—For this element, by the oxide–chloride method, Vichers, Hopkins, and Balke (*J. Amer. Chem. Soc.*, 1918, **40**, 615) obtained values ranging from $Er = 168.00$ to 168.84. The method of determination is thus again shown to be untrustworthy.

Thorium.—In a long series of concordant analyses of thorium bromide, Hönigschmid (*Zeitsch. Elektrochem.*, 1916, **22**, 18) finds $Th = 232.152$ from the silver ratio and 232.150 from the silver chloride ratio when $Br = 79.916$. The value $Th = 232.15$ should be adopted for general use. He also studied thoria from uranium ores which contained ionium. For this mixture, he obtained an atomic weight slightly in excess of 231.50. This may be approximate to the unknown atomic weight of ionium.

K K* 2

Uranium.—The latest series of determinations of the atomic weight of uranium by Hönigschmid and Horovitz (*Monatsh.*, 1916, **37**, 185) was based, like their earlier series, upon analyses of the tetrabromide. Two sets of analyses were made, one upon a bromide which had been fused in bromine vapour, the other in nitrogen. The value obtained ranged from $U = 238·04$ to $238·16$, the latter being in harmony with their former determinations. The rounded figure, $238·2$, is given in the table.

Helium.—Taylor (*Physical Rev.*, 1917, **10**, 653), using the micro-balance in determining the density of helium, finds $He = 4·0008$. Guye (*J. Chim. Phys.*, 1918, **16**, 46), in a recalculation of the data, finds $He = 3·998$. The value 4 should be retained.

Argon.—From the density and compressibility of argon, Leduc (*Compt. rend.*, 1918, **167**, 70) finds $A = 39·91$. He regards the second decimal as uncertain, and advises the adoption of the rounded value $39·9$.

In the following table of atomic weights proposed for 1920, few changes have been made from the values given in the last preceding table. The new values are: $A = 39·9$, $B = 10·9$, $Ga = 70·1$, $Th = 232·15$, and $Yt = 89·33$. In addition to these, the atomic weight of nitrogen should be changed from $14·01$ to the more precise value $N = 14·008$. The latter figure represents all the best determinations, and is probably correct to within 1 in the third decimal place. For so small a value, the change is insignificant.

(*Signed*) F. W. CLARKE.
T. E. THORPE.
G. URBAIN.

1920.

International Atomic Weights.

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·9	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·68
Barium	Ba	137·37	Niton (radium emanation)	Nt	222·4
Bismuth	Bi	208·0	Nitrogen	N	14·008
Boron	B	10·9	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·00	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·9
Chlorine	Cl	35·46	Radium	Ra	226·0
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·1	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
Erbium	Er	167·7	Selenium	Se	79·2
Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	70·1	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·06
Glucinum	Gl	9·1	Tantalum	Ta	181·5
Gold	Au	197·2	Tellurium	Te	127·5
Helium	He	4·00	Terbium	Tb	159·2
Holmium	Ho	163·5	Thallium	Tl	204·0.
Hydrogen	H	1·008	Thorium	Th	232·15
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	118·7
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·84	Tungsten	W	184·0
Krypton	Kr	82·92	Uranium	U	238·2
Lanthanum	La	139·0	Vanadium	V	51·0
Lead	Pb	207·20	Xenon	Xe	130·2
Lithium	Li	6·94	Ytterbium (Neoytterbium)	Yb	173·5
Lutecium	Lu	175·0	Yttrium	Yt	89·33
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·6			

LXXIII.—*The Presence of Aconitic Acid in Sugar-cane Juice and a New Reaction for the Detection of the Acid.*

By CHARLES SOMERS TAYLOR.

AMONG the non-saccharine substances existing in sugar-juice, Geerligs mentions certain acids which are undoubtedly present. He states, however, that the question of the presence of aconitic acid requires further investigation (" Cane Sugar and the Process of its Manufacture," 1909, p. 51). This acid is generally supposed to have been detected first in the juice of the sugar-cane by Behr (*Ber.*, 1877, **10**, 351). There is no doubt that Behr discovered large quantities of aconitic acid in muscovado sugar and molasses, from both of which he obtained the acid, the composition of which he verified by combustion and also by the formation of a silver salt of known composition. He also appears to have examined the action of lime on invert-sugar in order to find whether the acid can have been formed in the process of manufacture, and states that none of the acid was produced in any of his experiments. As the latter evidence was merely negative, however, he obtained from Cuba some sugar-juice sterilised with phenol, which he examined in Germany. His deduction that aconitic acid was present in this sugar-cane juice was based on the fact that he obtained the lead and acid ammonium salts in their characteristic form. The real criteria of analysis and melting-point determinations were omitted, and he lost the cleanest portion of his acid by accident, whilst some of the partly clean substance obtained by him melted at 167°, or more than 20° below the true melting point of aconitic acid. His evidence, therefore, of the actual existence of this acid in quantity in the juice in its natural state appeared to require further corroboration before it could be said to be conclusive.

The most interesting point to the sugar manufacturer as regards the existence of this acid is that it forms a calcium salt which dissolves readily in cold water, but is almost entirely insoluble in hot. It is therefore liable to be precipitated on the tubes of the evaporating plant unless care is taken to keep the juice hot while filtering.

EXPERIMENTAL.

As it was thought possible that the acid might be a product of disease in the cane, two samples of juice were employed, one from

diseased and one from ordinary cane. Both samples were precipitated with basic lead acetate. The precipitate was then washed, suspended in water, and decomposed in the usual manner with hydrogen sulphide. After filtration, the water was evaporated in a vacuum, and the crystalline residue extracted with ether. The portion insoluble in ether was mostly malic acid. The crude aconitic acid from the ethereal solution was purified by reprecipitating with lead acetate and decomposing the precipitate with hydrogen sulphide. Small quantities of aconitic acid were obtained from the juice of the ordinary canes, but the diseased canes gave a viscid substance by this treatment, from which it was found impossible to crystallise the acid.

Examination of the Acid.—The mean of two determinations of the equivalent weight of the acid gave the value 58·55. The quantities taken were very small, so that the method was subject to large error.

The acid melted and decomposed at 191° (corr.), which is the melting point of aconitic acid. (Found: $C=41·38$; $H=3·95$ *; $C=41·01$; $H=3·65$. $C_6H_6O_6$ requires $C=41·38$; $H=3·45$ per cent.)

Qualitative Experiments: A New Colour Test for Aconitic Acid and, indirectly, for Citric Acid.

The usual qualitative tests were carried out with the acid in order to identify it as aconitic acid, although these tests had already been performed by Behr. The calcium salt was obtained as a heavy, white precipitate on boiling a solution of the sodium salt with calcium chloride. It was interesting to note that unless the boiling was protracted, this precipitate dissolved immediately on cooling. After protracted boiling, however, the gelatinous precipitate appeared to change into a crystalline form, which was insoluble even after cooling.

A very delicate test for aconitic acid was discovered in examining the action of acetic anhydride on it. On the addition of this reagent to a small quantity of the acid, a pink coloration appeared, which rapidly turned to deep red and then to magenta. Further heating produced a bluish-green liquid, finally turning to a brown, almost opaque, solution. The red liquid first obtained, if the action is checked by cooling, shows a spectrum entirely in the red, absorbing all other rays almost completely. In the intermediate

* This abnormally high result for hydrogen was probably due to the fact that the combustion was made in India in the middle of the rains, on a day when the air was nearly saturated.

stage, when the magenta liquid was obtained, it appeared to consist
of a solution of two coloured substances, namely, a red one which
was soluble in water and a blue one which dissolved readily in ether.
The two could be easily separated by shaking the acetic anhydride
solution with water and ether, when the aqueous layer became red
and the ethereal solution blue.

Many attempts were made to isolate these red and blue com-
pounds, but they appear to be exceedingly unstable, being rapidly
destroyed by water, acids, or alkalis.

The substance obtained in this way is intensely highly coloured.
The intensity of the colour is so great, in fact, that the faintest
trace of aconitic acid will produce a strong colour. The minimum
quantity necessary to obtain the colour was determined as follows.

One gram of aconitic acid was dissolved in a litre of water, and
various fractions of a milligram were obtained by appropriate
dilutions and evaporation to dryness in porcelain basins. To the
residue a few drops of acetic anhydride were added, and the whole
was heated on a water-bath. The results are tabulated below:

Aconitic acid. Milligram.	Colour obtained.
1·0	Intense, appearing almost immediately.
0·1	Strong tinge rather slower in appearance.
0·02	Faint colour taking some time to appear.
0·01	Faint colour just perceptible after some time.

That this reaction was due to aconitic acid alone, and not to
the other acids present in sugar-cane juice, was proved positively
by examining pure aconitic acid from another source, which gave
the same results as that obtained from sugar-cane juice. It was
also proved negatively by showing that none of the other acids
present in sugar-cane gives the reaction. Citric acid, however, may
be detected by the action of acetic anhydride after gentle fusing
in a test-tube. By this means, traces of aconitic acid are obtained
which at once give the colour reaction. Citric acid itself does not
give the reaction.

By this colour test, it was also proved that aconitic acid exists
as a salt in sugar-cane juice, and not in the free state. This was
done by shaking with ether sugar-cane juice; in the ordinary state
and after treatment with dilute sulphuric acid. The ethereal
extract in both cases was evaporated to dryness, and the residue
heated on a water-bath with acetic anhydride. The extract from
the untreated juice gave no reaction whatever, whilst that from
the juice which had been treated with sulphuric acid gave the
intense red characteristic of aconitic acid.

The Nature of the Colour Reaction between Acetic Anhydride and Aconitic Acid.

That the colour reaction takes place by condensation of the carboxyl groups of the acid is almost certainly proved by the fact that ethyl aconitate, when treated with acetic anhydride, gives no colour whatever.

Treatment of itaconic, citraconic, and mesaconic acids also gave no colour. It was therefore inferred that very little decomposition of the molecule takes place during the reaction, but that the change was probably one of rearrangement of the carbon atoms with, possibly, some removal of water, addition of acetic anhydride, or both actions together.

As has been already mentioned, the actual coloured substance is extremely unstable. Evaporation of the acetic anhydride solution in a vacuum over sodium hydroxide, and subsequent washing with ether, gives a brown substance, which appears to be microcrystalline. No definite crystals were obtained. Analysis of this brown substance gave the following figures:

Found: $C = 51·63$; $H = 2·93$.

$C_6H_4O_4$ requires $C = 51·43$; $H = 2·86$ per cent.

The substance does not appear to resemble any of the known compounds of this formula. Its deep yellowish-brown colour resembles that of $2:5$-dihydroxybenzoquinone, but it appears to be more unstable than that substance. All that can be said for the present, therefore, is that the brown substance has many properties which would point to its having a quinonoid structure, but that this is not proved.

LABORATORY OF THE AGRICULTURAL CHEMIST
TO THE GOVERNMENT OF BIHAR AND ORISSA.

[*Received, January 6th, 1919.*]

LXXIV.—*Studies in the Camphane Series. Part XXXVII. Aryl Derivatives of Imino- and Amino-camphor.*

By MARTIN ONSLOW FORSTER and HANS SPINNER.

THE highest recorded molecular rotation is that of *p*-phenylenebis-iminocamphor, which has $[M]_D$ $6173°$ in a pyridine solution containing $0·624$ gram in 100 c.c. (Forster and Thornley, T., 1909, **95**, 942). In this compound there appears to be presented, within a relatively

narrow molecular compass, the optimum association of azethenoid groups, conjugated linkings, and a benzene ring,

$$C_8H_{14} \diagdown \!\!\! \stackrel{\displaystyle C:N \cdot C_6H_4 \cdot N:C}{\underset{\displaystyle C:O \qquad O:C}{|}} \!\!\! \diagup C_6H_{14},$$
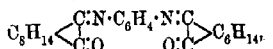
required for exaltation of the optical activity due originally to the camphor nucleus.

With a view to extending this field of inquiry we prepared a selection of similar compounds, but since none of these, with one exception, approached the foregoing substance in optical activity, they have been described only in a dissertation (Hans Spinner, Zürich, 1912). Several of them having now been prepared by Singh and Mazumder (this vol., 566), who did not have access to the publication in question, we desire to record the properties of the remainder.

The only derivative of this class having optical activity nearly so high as that displayed by p-phenylenebisiminocamphor is pp-diphenylenebisiminocamphor,

$$C_8H_{14} \diagdown \!\!\! \stackrel{\displaystyle C:N \cdot C_6H_4 \cdot C_6H_4 \cdot N:C}{\underset{\displaystyle C:O \qquad\qquad O:C}{|}} \!\!\! \diagup C_8H_{14},$$
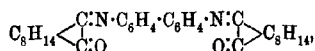
prepared from benzidine and camphorquinone. It occurs in two forms, (1) yellowish-green, melting at 276° and having $[M]_D$ 5565°, and (2) golden-brown, melting at 274° with $[M]_D$ 5360°. In this compound the same exaltation factors are noticeable, but they operate in a slightly less confined molecular environment, which may account for the somewhat diminished optical activity.

It has not been possible permanently to convert either of these compounds into the corresponding derivative of aminocamphor, but the substituted iminocamphors of more simple structure are easily so converted; there is then observed the same profound depression in optical activity already noticed in similar examples (F. and T., *loc. cit.*), as indicated by the following measurements in chloroform at 20°:

	$[a]_D.$	$[M]_D.$	Difference of $[M]_D.$
a-Naphthyliminocamphor	628°	1828°	—
a-Naphthylaminocamphor	115	338	1490°
β-Naphthyliminocamphor	720	2096	—
β-Naphthylaminocamphor	140	411	1685
o-Chlorophenyliminocamphor ...	153	423	—
o-Chlorophenylaminocamphor ...	94	262	161
m-Chlorophenyliminocamphor ...	499	1374	—
m-Chlorophenylaminocamphor ...	118	328	1046
m-Carboxyphenyliminocamphor .	470	1341	—
m-Carboxyphenylaminocamphor .	127	364	975
p-Carboxyphenyliminocamphor...	423	1205	—
p-Carboxyphenylaminocamphor	121	347	858

The one exception is *o*-chlorophenyliminocamphor, because it has by far the lowest optical activity yet recorded in this series, namely, $[M]_D\ 423°$, whilst none of the other members, even the *m*- or *p*-chloro-derivative, has $[M]_D$ less than 1000°; it is probable that this abnormality is due to partial saturation of the azethenoid or carbonyl group by supplemental valency of the chlorine atom in an ortho-position.

Although arylamines generally undergo condensation with camphorquinone very readily, some exceptions, in addition to that of *p*-nitroaniline, have been observed; these are *o*-aminobenzoic acid, *o*-aminophenol, 2:4-diaminophenol, 2:4:6-triaminophenol, picramide, picramic acid, 4-nitro-*α*-naphthylamine, and 5-nitro-*α*-naphthylamine, from none of which has the corresponding derivative of iminocamphor been obtained.

<div align="center">EXPERIMENTAL.</div>

$$\text{α- and β-Naphthylaminocamphor, } C_8H_{14}{<}^{CH\cdot NH\cdot C_{10}H_7}_{CO}.$$

α-Naphthyliminocamphor, with $[α]_D\ 628·2°$ in chloroform, also prepared by Singh and Mazumder (this vol., 573), was shaken in ethereal solution with 10 per cent. potassium hydroxide and zinc dust until the colour had disappeared, when the ether deposited a white residue of *α*-naphthylaminocamphor on evaporation. Recrystallisation from hot alcohol gave transparent, four-sided prisms melting at 165°:

0·1760 gave 0·5276 CO_2 and 0·1251 H_2O. C = 81·76; H = 7·90.

$C_{20}H_{23}ON$ requires C = 81·91; H = 7·85 per cent.

The product is readily soluble in benzene, chloroform, ethyl acetate, or boiling acetone, moderately so in cold acetone or alcohol; it is insoluble in cold light petroleum, which dissolves it sparingly when boiled. A solution containing 0·1215 gram in 25 c.c. of chloroform gave $α_D\ 1°41'$ in the 3-dcm. tube, whence $[α]_D\ 115·5°$.

β-Naphthyliminocamphor, with $[α]_D\ 720·5°$ (compare S. and M., this vol., 573), was treated in the same way, and the resulting *β*-naphthylaminocamphor crystallised from alcohol in colourless, flattened, four-sided plates melting at 157—158°:

0·2305 gave 0·6896 CO_2 and 0·1631 H_2O. C = 81·59; H = 7·86.

The base is insoluble in cold light petroleum, but dissolves readily in other organic media. A solution containing 0·1255 gram in 25 c.c. of chloroform gave $α_D\ 2°7'$ in the 3-dcm. tube, whence $[α]_D\ 140·5°$.

o- *and* m-*Chlorophenylaminocamphor,* $C_8H_{14} <^{CH \cdot NH \cdot C_6H_4Cl}_{CO}$.

o-Chlorophenyliminocamphor, with $[\alpha]_D$ 153·4° (compare S. and M., this vol., 572), gave o-chlorophenylaminocamphor melting at 148° after crystallisation from hot alcohol, which deposits it in colourless, transparent prisms:

0·2174 gave 0·5508 CO_2 and 0·1431 H_2O.   C = 69·10; H = 7·31.
0·1982 ,,   0·1013 AgCl.   Cl = 12·64.
$C_{16}H_{20}ONCl$ requires C = 69·16; H = 7·26; Cl = 12·77 per cent.

It is readily soluble in organic media other than alcohol and petroleum, which dissolve it less freely. A solution containing 0·1236 gram in 25 c.c. of chloroform gave α_D 1°24′ in the 3-dcm. tube, whence $[\alpha]_D$ 94·4°.

m-Chlorophenyliminocamphor, with $[\alpha]_D$ 498·8° (S. and M., *loc. cit.*), gave m-chlorophenylaminocamphor melting at 98—99° after crystallisation from diluted alcohol, whence it separates in colourless aggregates of indefinite structure:

0·1726 gave 0·4368 CO_2 and 0·1129 H_2O.   C = 69·02; H = 7·27.
0·2158 ,,   0·1106 AgCl.   Cl = 12·68.

It is more readily soluble than the isomeride. A solution containing 0·1234 gram in 25 c.c. of chloroform gave α_D 1°45′ in the 3-dcm. tube, whence $[\alpha]_D$ 118·2°.

m- *and* p-*Carboxyphenyliminocamphor,* $C_8H_{14} <^{C:N \cdot C_6H_4 \cdot CO_2H}_{CO}$.

Camphorquinone and m-aminobenzoic acid in molecular proportion were heated in alcohol during three hours, when the product, after recrystallisation from diluted alcohol, formed pale yellow leaflets melting at 195·5°:

0·3273 gave 15·4 c.c. N_2 at 29° and 763 mm.   N = 5·21.
$C_{17}H_{19}O_3N$ requires N = 4·91 per cent.

It is readily soluble in alcohol, acetone, chloroform, ethyl acetate, or boiling benzene, but is insoluble in light petroleum. A solution containing 0·1218 gram in 25 c.c. gave α_D 4°35′ in the 2-dcm. tube, whence $[\alpha]_D$ 470·4°.

The isomeride prepared from camphorquinone and p-aminobenzoic acid separated from diluted alcohol in small, brownish-yellow prisms melting at 237°, and resembling the m-compound in solubility:

0·4210 gave 19·0 c.c. N_2 at 21° and 758 mm.   N = 5·15.

A solution containing 0·1217 gram in 25 c.c. of chloroform gave α_D 4°7′ in the 2-dcm. tube, whence $[\alpha]_D$ 422·8°.

m- *and* p-*Carboxyphenylaminocamphor*, $C_8H_{14} \diagdown \begin{smallmatrix} CH \cdot NH \cdot C_6H_4 \cdot CO_2H \\ | \\ CO \end{smallmatrix}$.

The foregoing substances dissolve in aqueous alkali hydroxide, and when the solutions are shaken with zinc dust, filtered, and acidified, the corresponding derivative of aminocamphor is liberated. The m-compound separates from diluted alcohol in colourless needles melting at 210—211°!

0·1630 gave 0·4237 CO_2 and 0·1075 H_2O. C = 70·89; H = 7·33.

$C_{17}H_{21}O_3N$ requires C = 71·08; H = 7·32 per cent.

It dissolves readily in acetone, chloroform, or ethyl acetate, less readily in alcohol, being only moderately soluble in benzene and insoluble in petroleum. A solution containing 0·1235 gram in 25 c.c. of chloroform gave a_D 1°53′ in the 3-dcm. tube, whence $[a]_D$ 127·1°.

The p-compound crystallises from diluted alcohol in colourless aggregates melting at 239° after slight shrinking and discoloration:

0·1951 gave 0·5081 CO_2 and 0·1287 H_2O. C = 71·03; H = 7·33.

In solubility it resembles the isomeride. A solution containing 0·1207 gram in 25 c.c. of chloroform gave a_D 1°45′ in the 3-dcm. tube, whence $[a]_D$ 120·8°.

p-*Acetylaminophenyliminocamphor*, $C_8H_{14} \diagdown \begin{smallmatrix} C:N \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3 \\ | \\ CO \end{smallmatrix}$.

Camphorquinone and p-aminoacetanilide in molecular proportion dissolved in alcohol were heated under reflux during four hours, the product crystallising on dilution in yellow, six-sided plates melting at 211—212°:

0·2166 gave 17·8 c.c. N_2 at 21° and 771 mm. N = 9·53.

$C_{18}H_{22}O_2N_2$ requires N = 9·40 per cent.

It is readily soluble in alcohol, acetone, chloroform, or ethyl acetate, dissolving with difficulty in cold benzene or hot petroleum; it is insoluble in the last-named when cold. A solution containing 0·1220 gram in 25 c.c. of chloroform gave a_D 8°25′ in the 2-dcm. tube, whence $[a]_D$ 862·4° and $[M]_D$ 2570°.

pp-*Diphenylenebisiminocamphor*,

$C_8H_{14} \diagdown \begin{smallmatrix} C:N \cdot C_6H_4 \cdot C_6H_4 \cdot N:C \\ | \quad\quad\quad\quad | \\ CO \quad\quad\quad OC \end{smallmatrix} \diagup C_8H_{14}$.

Camphorquinone (6·6 grams) and benzidine (3·6 grams) dissolved in alcohol (80 c.c.) were heated under reflux during six hours, when the liquid deposited two distinguishable forms of crystals on cooling;

these were separated mechanically and also by fractional crystallisation, when the less soluble component, formed in preponderating amount, consisted of longitudinal clusters of minute, yellowish-green prisms melting at 276° :

0·2599 gave 0·7606 CO_2 and 0·1785 H_2O. C = 79·81 ; H = 7·63.

0·2680 „ 13·4 c.c. N_2 at 22° and 765 mm. N = 5·73.

$C_{32}H_{36}O_2N_2$ requires C = 80·00 ; H = 7·50 ; N = 5·83 per cent.

A solution containing 0·1231 gram in 25 c.c. of chloroform gave a_D 11°25' in the 2-dcm. tube, whence $[a]_D$ 1159·3°.

The more readily soluble modification crystallised in transparent, golden-brown needles melting at 274° :

0·1861 gave 0·5458 CO_2 and 0·1288 H_2O. C = 79·98 ; H = 7·69.

A solution containing 0·1220 gram in 25 c.c. of chloroform gave a_D 10°54' in the 2-dcm. tube, whence $[a]_D$ 1116·8°. Both forms yielded benzidine and camphorquinone on hydrolysis with alcoholic hydrochloric acid.

In addition to the foregoing substances we prepared o- and p-tolyliminocamphor and p-benzeneazophenyliminocamphor, which are described by Singh and Mazumder, and in the case of the last-named compound a discrepancy is noticeable. These authors obtained orange needles melting at 129—130° and giving $[a]_D$ 550·4° in chloroform, whilst our product crystallised in silky, red needles melting at 135° and giving $[a]_D$ 677·0°, whence $[M]_D$ 2335°.

p-*Benzeneazophenylaminocamphor*,

$$C_8H_{14} \diagdown \genfrac{}{}{0pt}{}{CH \cdot NH \cdot C_6H_4 \cdot N:N \cdot C_6H_5}{CO}$$
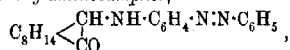
was obtained by shaking an ethereal solution of the iminocamphor derivative with zinc dust and 10 per cent. potassium hydroxide in a closed flask during several hours, when the colour was completely destroyed. On contact with air, however, the ethereal liquid immediately became orange, and on evaporation deposited a brownish-red mass which crystallised from alcohol in lustrous, dark brownish-red, three-cornered plates melting at 170° :

0·1272 gave 0·3538 CO_2 and 0·0826 H_2O. C = 75·86 ; H = 7·21.

$C_{22}H_{25}ON_3$ requires C = 76·08 ; H = 7·20 per cent.

From these colour changes it would appear that benzeneazophenyliminocamphor (I) is first reduced to the colourless phenylhydrazinophenylaminocamphor (II ; not isolated), which is then oxidised in air

$$C_8H_{14} \diagdown \genfrac{}{}{0pt}{}{C:N \cdot C_6H_4 \cdot N:N \cdot C_6H_5}{CO}$$ $$C_8H_{14} \diagdown \genfrac{}{}{0pt}{}{CH \cdot NH \cdot C_6H_4 \cdot NH \cdot NH \cdot C_6H_5}{CO}$$

(I.)   (II.)
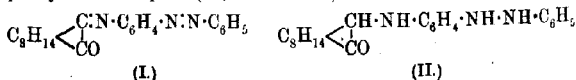
to benzeneazophenylaminocamphor. Even very dilute solutions of the last-named substance were too dark for polarimetric measurement.

These experiments were carried out at the Royal College of Science, South Kensington, during the later months of 1911.

SALTERS' HALL,
ST. SWITHIN'S LANE, E.C. 4.   [*Received, July 3rd,* 1919.]

LXXV.—*The Oxidation of Coal.*

By FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER.

IN a recent paper ("The Oxidation and Ignition of Coal," T., 1918, 113, 945) a hypothesis was advanced that the first step in the oxidation of coal is the formation of an additive compound, or complex, of oxygen with one or more of the substances present in coal.

Partington (*Chem. News,* 1919, 118, 50) has suggested "that this hypothesis, which is of itself not very probable, does not account for the observed results, and that it should be replaced by another hypothesis," based primarily on known physical phenomena, which appears to be somewhat as follows.

(1) The admission of air to newly-won coal, deprived of its occluded gases, results in the physical adsorption of both oxygen and nitrogen on the surface of the coal. The pressure of the air in contact with the coal will at first fall very rapidly for a short period, and will then gradually fall off until adsorption equilibrium is reached. If the adsorbed layer penetrates into the bulk of the adsorbent, this very slow final fall of pressure may go on for a long time.

(2) The adsorbed layer, being at high concentration, may subsequently react with the coal, possibly slowly, with the production of oxides of carbon.

(3) The formation of carbon monoxide and carbon dioxide in a constant ratio at a given temperature is explained on the assumption that carbon monoxide is formed first and subsequently reacts with water-vapour, the "water-gas equilibrium," $CO + H_2O \rightleftharpoons CO_2 + H_2$, being attained.

This hypothesis in principle possesses the great merits of simplicity and of conformity with well-known phenomena. Had it been

possible to account so easily for the facts observed during the oxidation of coal, some such hypothesis would have been chosen in preference to that ultimately adopted.

The phenomena that occur during the oxidation of coal bear a striking resemblance to, and clearly have much in common with, the phenomena of the combustion of carbon.

Rhead and Wheeler (T., 1913, **103**, 461) were faced with a similar difficulty to that which presents itself with coal when attempting to explain the results of their experiments on the combustion of carbon. They found that carbon at all temperatures up to 900°, and probably above that temperature, has the power of pertinaceously retaining oxygen. This oxygen cannot be removed by exhaustion alone, but only by increasing the temperature of the carbon during exhaustion. When quickly released in this manner, it appears, not as oxygen, but as carbon monoxide and carbon dioxide. Rhead and Wheeler concluded, after discussion of their experimental data at some length, that: " No physical explanation alone can account for this ' fixation ' of oxygen, but, in all probability, it is the outcome of a physico-chemical attraction between oxygen and carbon. Physical, inasmuch as it seems hardly possible to assign any definite molecular formula to the complex formed, which, indeed, shows progressive variation in composition; chemical, in that no isolation of the complex can be effected by physical means."

In an account of earlier portions of the same research (T., 1912, **101**, 846), the relationship between the carbon monoxide and carbon dioxide produced during the oxidation of carbon had been fully discussed. A comparison of the rates of reaction at different temperatures, between carbon and carbon dioxide, carbon and oxygen, and carbon monoxide and oxygen, with a study of the products of reaction, showed: (1) that some carbon monoxide is produced during the oxidation of carbon at low temperatures under conditions which do not admit of the reduction of carbon dioxide by carbon; on the other hand, (2) carbon dioxide is produced at low temperatures in quantity greater than can be accounted for on the supposition that carbon monoxide is first formed and then oxidised to carbon dioxide. The conclusion follows that when carbon is burnt at low temperatures, carbon monoxide and carbon dioxide are produced simultaneously.

The general conclusion reached by Rhead and Wheeler as regards the mode of combustion of carbon, to account for this simultaneous production of the two oxides, presumes the formation of a complex, as already stated, and partial decomposition of this complex as fresh oxygen molecules became attached, until the carbon becomes "saturated." The products of combustion during this period of satura-

tion are the complex, carbon dioxide, and carbon monoxide. After the carbon has become saturated there is an alternate formation and decomposition of the complex, and the only apparent products of combustion are carbon dioxide and carbon monoxide. These are produced in a fixed ratio dependent on the temperature of reaction. Drying of the oxygen by phosphoric oxide does not affect the formation of the complex, but retards its rate of decomposition (T., 1913, 103, 1310).

This explanation of the manner of burning of carbon is, we believe, accepted by the majority of chemists. A similar explanation of the manner of burning of coal at low temperatures could be advanced by analogy. To rely solely on such an analogy is, however, scarcely safe; for although there are, in all probability, compounds in coal resembling the carbon molecule in their structure (see Jones and Wheeler, T., 1916, 109, 709), there is no evidence of the presence of free carbon. Moreover, the fact that the compounds in coal are hydrogenated and that some may yield water on oxidation, introduces a complication from which research on the combustion of carbon is free.

Nevertheless, if the same methods of examining the action of oxygen on coal be followed as with carbon, a similar conclusion will be reached : an hypothesis of physical adsorption of the oxygen, followed by direct formation of carbon monoxide, and, subsequently, of carbon dioxide is inadequate to explain quantitatively the results obtained ; although it may, at first sight, afford a plausible explanation of the phenomena qualitatively.

A comparison of the amount of adsorption of inert gases, such as nitrogen, by coal with the amount of oxygen absorbed thereby shows the two actions to be not only of a different order but to be affected by temperature in a different sense.

The adsorption of gases by coal has been studied by several chemists; for example, Graham (*Trans. Inst. Min. Eng.*, 1917, 52, 388) and Katz (*U.S. Bureau of Mines, Tech. Paper* 147 ; Washington, 1917). Graham obtained the following figures for the quantities of different gases adsorbed or, as he terms it, "dissolved," by the same sample of coal-dust (of 200-mesh fineness) :

Volume of gas adsorbed per gram of coal.
C.c measured at N.T.P.

Temperature.	H_2.	N_2.	CO.	CH_4.	CO_2.
30°	0·068	0·576	0·712	—	8·00
100°	0·038	0·115	0·159	0·476	1·48

As regards oxygen, Graham's own words may be quoted : "The solubility of oxygen—as distinct from the ordinary (chemical) absorption by coal—has also been determined for a sample of

oxidised coal-dust, it being, of course, impossible to determine the solubility in unoxidised coal directly. The sample used had been oxidised for about fourteen days at 100°, and even after this a slight absorption at 30° still took place. For this, however, a correction could be made, and with this it was found that oxygen was soluble in the oxidised sample of coal-dust (of 200-mesh fineness) to the extent of about 40 c.c. per 100 gram when the percentage of oxygen over the dust equalled 100. The solubility of nitrogen in the same sample was found to be equal to approximately 35 c.c. for

FIG. 1.

Time in hours.
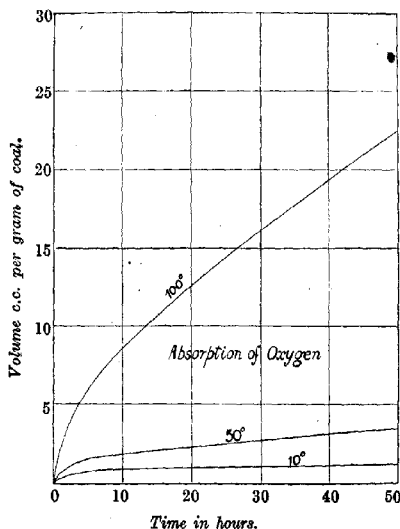
100 per cent. nitrogen per 100 gram of coal. The figure for the solubility of nitrogen in unoxidised coal for similar concentration was 57·6. It is highly probable, therefore, that the solubility of oxygen in unoxidised coal will be somewhere about 65 c.c. in pure oxygen per 100 gram of coal."

These results for different gases are in agreement with the determinations made of the adsorption of gases by charcoal by Homfray (*Zeitsch. physikal. Chem.*, 1910, **74**, 129), who showed that the amounts adsorbed are proportional to the boiling points of the gases.

In Fig. 1 are given time-volume curves for the absorption of

oxygen by fresh coal (of 10-mesh fineness and deprived of its occluded gases) at 10°, 50°, and 100°; and in Fig. 2 the same curves are reproduced on a different scale for comparison with adsorption curves for nitrogen at 30°, 50°, and 100°. The nitrogen curve at 50° was obtained with a sample of the same coal as was used for the absorption of oxygen; the curves at 30° and 100° are constructed from Graham's data (obtained with a coal of 200-mesh fineness).

Increase of temperature is thus shown to cause a rapid increase in

FIG. 2.
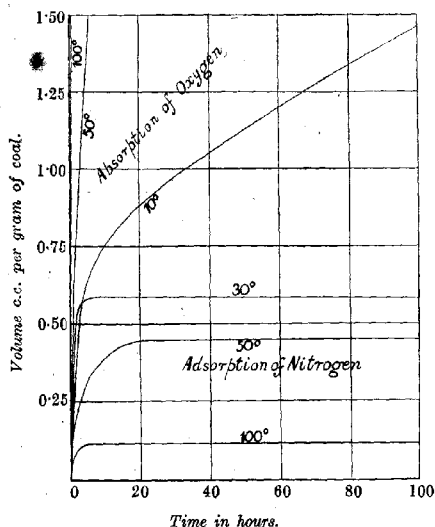
the rate of absorption of oxygen by coal, and an increase in the total amount absorbed (compare also Winmill, *Trans. Inst. Min. Eng.*, 1913, **46**, 3, 559; 1914, **48**, 514). On the other hand, the quantity of a gas physically adsorbed decreases as the temperature is increased.

Even at the ordinary atmospheric temperature the amount of absorption of oxygen by coal is greater than can be accounted for by adsorption phenomena; and the higher the temperature the greater the divergence. Hence the necessity for some such hypothesis as that of complex-formation to account for the facts. Undoubtedly, it is the small but continually renewed amount of

adsorbed oxygen which forms the complex; as with all heterogeneous reactions, the reaction takes place in the condensed layer at the boundary between the two phases; but the complex-formation, and not the adsorption, is specific of the reaction between coal and oxygen.

It is, perhaps, necessary to answer the arguments brought forward in favour of the production of carbon dioxide through the agency of water-vapour, either from carbon monoxide or by direct action on the coal.

The suggested reactions are: $CO + H_2O \longrightarrow CO_2 + H_2$; $C + 2H_2O \longrightarrow CO_2 + H_2$; and, possibly, $2H_2 + O_2 \longrightarrow 2H_2O$. Each of these reactions is known normally to proceed but slowly at temperatures below 400°. With the high concentration of the gases on the coal surface it is conceivable that they might be appreciable at 100° or lower. No such reactions occur during the oxidation of carbon at low temperatures, but, as already indicated, it is desirable not to stress the similarity between coal and carbon. Experiments were therefore made with coal, which showed:

(1) That no trace of hydrogen could be detected in oxygen which had been circulated over coal at 100° during several days.

(2) That (moist) mixtures of carbon monoxide and air circulated over coal at 100° suffered no change other than that due to the action of oxygen on the coal. No hydrogen was formed.

(3) That mixtures of hydrogen and air circulated over coal at 100° suffered no loss of hydrogen.

In each set of experiments the usual formation of carbon dioxide and carbon monoxide, in the ratio $2.4 : 1$, took place.

Partington has suggested that "if the reaction between oxygen and coal were one of combination, with the formation of a complex oxide of carbon," the complex should have a definite univariant relationship between vapour pressure and temperature. The complex is not regarded as a definite oxide of carbon or of coal; there most probably are slightly differing compounds in coal to which the oxygen attaches itself, each forming a slightly different product. Probably, also, these oxygen-fixing compounds, which appear to be derived from the cellulosic portions of the original coal-forming materials, have no definite molecular dimensions, but are continuous in structure. The effect of progressive increase of temperature on the complex formed with oxygen by such compounds would be to cause progressive breakdown of their structure with elimination of the simple oxides, the residue requiring further increase in temperature to decompose it further.

EXPERIMENTAL.

The results herein recorded were obtained during the course of, an investigation which is still in progress (and, when completed, will form the subject of a communication to this Society), on the relative tendencies to spontaneous ignition of the several distinct portions into which a banded bituminous coal can be separated (see Stopes, *Proc. Roy. Soc.*, 1919, [*B*], **90**, 470; Tideswell and' Wheeler, this vol., 619). The particular coal used was the "durain" portion of the Thick Coal Seam, Hamstead Colliery.

The apparatus used, which will be described in detail when the complete research is described, enabled air or oxygen or any mixture of gases to be circulated in a closed system through the coal, which was packed in a reaction-tube the temperature of which could be maintained constant. The progress of the reaction could be followed by the change of pressure within the system and by analysis of the gases.

In all but the experiments with mixtures of carbon monoxide and air, in which a water-bubbler was used, the gases were dried by passage through a calcium chloride tube included in the circuit. The coal was ground so as to pass through a 10×10 and remain on a 60×60 mesh sieve. At the beginning and end of each experiment the coal, in position in the reaction tube, was raised to $200°$ and exhausted at that temperature.

Typical results for the absorption of pure oxygen at different temperatures are recorded in Fig. 1. Typical results when mixtures of carbon monoxide and air and hydrogen and air were used are as follow :

Carbon Monoxide and Air ($7·45$ per cent. CO).

Volume of apparatus : $3,300$ c.c.
Mean pressure of gases : 660 mm.
Composition : Expressed as c.c. at $15°$ and 760 mm.

	CO_2.	O_2.	CO.	N_2.	H_2.
Initial atmosphere.........	$0·9$	590	227	2240	nil
Final atmosphere (after circulation during 120 hours at $100°$)............	$53·4$	79	249	2240	nil

Oxygen absorbed $= 511$ c.c. CO_2 formed $= 52·5$ c.c.
CO formed $= 22$ c.c.   Ratio $CO_2/CO = 2·4$.

	CO_2.	O_2.	CO.	N_2.	H_2.
Gases removed from the coal by exhaustion at $200°$	$26·5$	nil	$7·7$	$0·3$	nil
Ratio CO_2/CO removed at $200°$......................	$3·3$				

     K K**

Hydrogen and Air (3·85· per cent. H_2).

Volume of apparatus : 1,200 c.c.
Mean pressure of gases : 560 mm.

Composition : Expressed as c.c. at 15° and 760 mm.

	CO_2.	O_2.	CO.	N_2.	H_2.
Initial atmosphere	nil	213·5	nil	788	40·2
After 20 hours at 100° ...	10·52	16·5	3·46	796	40·8
,, 42 ,, , ,, ...	11·20	4·9	4·60	791	39·7
,, 66 ,, ,, ...	12·00	2·6	4·77	791	40·5

Oxygen absorbed = 211 c.c. CO_2 formed = 12·0 c.c.
CO formed = 4·77 c.c.   Ratio CO_2/CO = 2·5.

	CO_2.	O_2.	CO.	N_2.	H_2.
Gases removed from the coal by exhaustion at 200°	3·7	nil	1·2	0·1	nil
Ratio CO_2/CO removed at 200°	3·1				

ESKMEALS,
    CUMBERLAND.

Organic Chemistry.

Electrolytic Preparation of Chloroform. JOSEF FEYER (*Zeitsch. Elektrochem.*, 1919, **25**, 115—145).—The electrolytic preparation of chloroform from alcohol and from acetone has been investigated under various conditions, particularly in solutions of alkali chlorides and chlorides of the alkaline earth metals. It is shown that the methods put forward in the literature for the electrolytic preparation of chloroform from acetone are inaccurate in their details on account of imperfect methods of analysis. It is also shown that the present methods of isolating the chloroform are imperfect; this applies both to the method of absorption of the chloroform in alcohol and to the distillation method. Both methods involve considerable loss of material. Pure chloroform can only be directly obtained by freezing it out of its mixture with hydrogen by means of solid carbon dioxide and ether. The present methods of electrolysis are inefficient, because the alkali produced in the process decomposes considerable quantities of chloroform. By using a neutralisation cathode, it is possible to prepare chloroform from acetone in yields amounting to 65% of the current. When platinum electrodes are used, a material yield of 75—80% is obtained with a current density of 1·1 amp./sq. cm. at the anode and 0·5 amp./sq. cm. at the cathode. The primary reaction in the electrolysis is the formation of hypochlorite, which is followed by the reaction $CH_3 \cdot CO \cdot CH_3 + 3HOCl = CHCl_3 + CH_3 \cdot CO_2H + 2H_2O$. Methyl ethyl ketone and higher ketones react in the same way with electrolytic hypochlorite. The method for the preparation of chloroform from alcohol put forward by Trechzinsky (A., 1907, i, 270) is criticised and shown to be inaccurate. In the case of alcohol, it is also possible by the introduction of a neutralisation cathode to obtain considerable yields of chloroform at temperatures between 25° and 35° when a current density of 1 amp./sq. cm. is used on the anode and 1·5 amp./sq. cm. on the cathode. A current yield of 77% and a material yield of 82% were obtained under these conditions. The maximum yield is obtained at temperatures between 25° and 30°. The preparation of chloroform from acetone or alcohol in calcium chloride solution only proceeds well when specially prepared nickel or copper cathodes are used. These electrodes are prepared by immersing ordinary nickel or copper electrodes in concentrated nitric acid for a few moments and then washing with water. Using these electrodes, a current yield of 71% and a material yield of 80% were obtained from acetone in calcium chloride, whilst with alcohol in calcium chloride the material yield was 99% and the current yield 90%. The formation of chloroform from alcohol occurs in three stages: first, an oxidation of the alcohol to aldehyde; secondly, a formation of hypochlorite; and thirdly, an interaction between the

aldehyde and the hypochlorite: (i) $CH_3 \cdot CH_2 \cdot OH + HOCl =$ $CH_3 \cdot CHO + H_2O + HCl$; (ii) $OH' + Cl_2 = H' + Cl' + ClO'$; (iii) $CH_3 \cdot CHO + 3HOCl = CHCl_3 + HCO_2H + 2H_2O$; (iv) $H \cdot CO_2H +$ $HOCl = CO_2 + H_2O + HCl$. It is shown that equation (i) is partly ⁕replaced by the reaction $CH_3 \cdot CH_2 \cdot OH + O = CH_3 \cdot CHO + H_2O$.

J. F. S.

Substitution by Halogens in the Aliphatic Series. Ossian Aschan (*Finska Kem. Medd.*, 1918, 10 pp.; from *Chem. Zentr.*, 1919, i, 221).—The catalytic influence of light on the process of chlorination probably depends on the formation of the complex, Cl_3, in illuminated chlorine. The catalysing action of water is attributed to the production of a hydrate, $H_2OCl_2 + nH_2O$, which only actually separates below $0°$, but is assumed to be capable of transitory existence at a higher temperature. The presence of water during chlorination is particularly advantageous in the treatment of readily volatile hydrocarbons. The method of moist chlorination has been applied in particular to substituted hydrocarbons, such as ethyl chloride, *iso*amyl chloride, ethylene chloride, chloroform, propyl bromide, ethylene bromide, ethyl iodide, toluene, and xylene.   H. W.

Organic Chemical Reagents. IV. The Preparation of Alkyl Iodides. Roger Adams and V. Voorhees (*J. Amer. Chem. Soc.*, 1919, **41**, 789—798).—The usual laboratory methods for the preparation of the alkyl iodides are unsuitable when dealing with large quantities of material. The rapid preparation of methyl, ethyl, *n*-butyl and *iso*amyl iodides (in quantities of 3—4 kilos.) according to a modification of Walker's method (T., 1892, **61**, 717) is fully described, along with a detailed account of the apparatus employed. *n*-Propyl iodide was prepared in smaller amount.

The suitable alcohol is heated in a large, round-bottomed flask of about 12 litres capacity with a mixture of approximately equal amounts of red and yellow phosphorus. The vapours evolved are condensed in contact with iodine, and are then returned to the flask. The use of a certain amount of yellow phosphorus is particularly advantageous, the reaction then being instantaneous and the colour of the iodine disappearing immediately on reaching the reaction flask. During the subsequent distillation of the alkyl iodides, the troublesome frothing which occurs when only red phosphorus is employed is absent. Further quantities of iodine can be introduced without dismantling the apparatus, and it is possible to prepare more than 6 kilos. of crude iodide in a day, using enough phosphorus and alcohol for four portions of iodine of $1\frac{1}{2}$ kilos. each. Five such apparatus can easily be run simultaneously, producing 30 kilos. of crude product in a day.

In the case of butyl and amyl alcohols, the reaction proceeds extremely readily, owing to the great solvent action of these compounds on iodine at their boiling point. A small amount of yellow

phosphorus is always left behind, but phosphonium compounds do not appear to be formed. The yields are in every case 90—100% of the theoretical.

In the preparation of the lower alkyl haloids, a large excess of alcohol may be used, but in the case of the higher alcohols this must be avoided, as otherwise difficulties arise in the purification of the product.
F. C.

Nitroethylene. HEINRICH WIELAND and EUKLID SAKELLARIOS (*Ber.*, 1919, **52**, [*B*], 898—904).—*Nitroethylene* can be prepared in 50% yield by the dehydration of β-nitroethyl alcohol by phosphoric oxide or sodium hydrogen sulphate; it is an almost colourless, mobile liquid, b. p. 98·5°, $D_{15}^{13·8}$ 1·073, the vapour of which violently attacks the eyes and throat. It readily undergoes polymerisation; this occurs slowly when the pure substance is preserved, more rapidly on exposure to light. The process is remarkably catalysed by water, so that a freshly prepared aqueous solution of the substance becomes cloudy almost immediately, and the separation of the polymeride is complete in a few minutes (the substance cannot be depolymerised to nitroethylene by heat); polymerisation is retarded by acid, but in these circumstances a slow reaction with water occurs, with formation of β-nitroethyl alcohol. With alkali, polymerisation occurs with explosive violence. Reduction with stannous chloride and hydrochloric acid yields acetaldehyde and hydroxylamine, whilst with zinc dust and acetic acid ethylamine is produced. Nitroethylene unites immediately with bromine in ethereal solution, yielding *nitroethylene dibromide*, colourless liquid, b. p. 97°/21 mm., and with aniline giving *N-β-nitroethylaniline*, $NHPh·CH_2·CH_2·NO_2$, colourless leaflets, m. p. 37° (the *hydrochloride* is described).

[With E. BLÜMICH.]—Attempts to prepare nitroethylene by the elimination of hydrogen bromide from bromonitroethane by methylalcoholic potassium hydroxide were unsuccessful, the products being potassium bromide, potassium nitrite, and the *potassium* salt of dinitroethane, shining, golden needles which explode at about 150°; *αα-dinitroethane* has b. p. 72°/12 mm. H. W.

The Specific Gravity and Refractive Power of Solutions of Glycerol. H. WOLFF (*Zeitsch. angew. Chem.*, 1919, **32**, 1, 148).—The author has determined the density and refractive indices of solutions in water of an extremely pure sample of glycerol, with the following results:

86% *Solution.*—D_{15}^{15} 1·2294, $n_D^{12·5}$ 1·4545, n_D^{15} 1·4537, $n_D^{17·5}$ 1·4533 ; change in refractive index per °C., 2·8 × 10^{-4}.

76·77% *Solution.*—$D_{15}^{13·8}$ 1·2043, D_{15}^{15} 1·2036, D_{15}^{22} 1·1998, the coefficient of expansion being 0·000463. $n_D^{12·5}$ 1·4401, n_D^{15} 1·43945, $n_D^{17·5}$ 1·4388 ; change in refractive index per °C. = 2·6 × 10^{-4}.

The results agree very closely with those contained in Gerlach's table, but not so closely with those of Lenz, Strohmer, and Skalweit, although there is fair agreement with the latter. J. S. G. T.

New Initial Materials for the Preparation of Allyl Compounds. OSSIAN ASCHAN (*Finska Kem. Medd.*, 1918, 3 pp., from *Chem. Zentr.*, 1919, i, 221).—A mixture of glycerol and formic acid (95%) is heated for four hours under reflux in the presence of a small quantity of ammonium chloride as catalyst, and the product is fractionally distilled. At above 190°, the glycerol diformin primarily formed breaks down into allyl formate, water, and carbon dioxide, and decomposition is complete at 260°. Allyl chloride is obtained in good yield when cold allyl formate containing 10% of dissolved zinc chloride is treated with hydrogen chloride and the mixture is subsequently heated on the water-bath.   H. W.

Action of Heat on the Alkali and Alkali-Earth Methyl Sulphates. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, 168, 1054—1056).—Potassium methyl sulphate when heated at 220°, rising slowly to 280°, is decomposed almost quantitatively into potassium pyrosulphate and methyl ether. At a slightly lower temperature sodium methyl sulphate behaves similarly, but at the higher temperature 7% of the salt is decomposed into sodium sulphate and methyl sulphate. This second reaction with the formation of the two sulphates is the principal one, and occurs below 200° in the case of calcium, barium, and lithium methyl sulphates, and slowly in the cold in a desiccator in the case of strontium methyl sulphate.   W. G.

Alcoholysis. AD. GRÜN, FRANZ WITTKA, and EMIL KUNZE (*Chem. Umschau Fett-Ind.*, 1917, 24, 15—16, 31—34; from *Chem. Zentr.*, 1919, i, 222—223).—The authors have investigated the direct conversion of fats into the ethyl esters of their fatty acids by boiling them with alcohol containing a small amount of mineral acid. Alcoholysis in an acid medium is found to be a consecutive process, thus showing that the hydrolysis of fats proceeds by separate steps in every case. Pure tristearin was obtained by the catalytic reduction of almond or sesame oil and removal of oleodistearin and free fatty acid by washing with light petroleum and boiling with alcohol. The best results were obtained when tristearin (100 parts) was heated for three hours with a 1% solution of sulphuric acid in absolute alcohol (150 parts). The product consisted of a mixture of mono-, di-, and tri-stearin and ethyl stearate, from which the tristearin could readily be removed by crystallisation from alcohol; the separation of the other components was effected after distillation of ethyl stearate under diminished pressure, and was best accomplished by a frequent change of solvent (alcohols in which monostearin is most readily, and light petroleum in which it is least readily, soluble). Three thousand grams of tristearin yielded 400 grams of unchanged material (after repeated alcoholysis of the fraction which had escaped action in the first treatment), 300 grams of distearin, 200 grams of monostearin, more than 1200 grams of ethyl stearate, and 600 grams of mixed frac-

tions.   The distearin fraction had m. p. 74·5°, 75°, 75·5° (it should be noted that a molar mixture of mono- and tri-stearin has the same m. p. as distearin); it was converted by thionyl chloride into distearochlorohydrin, m. p. 56°, described by Grün and Theimer, and appears to be the *αβ*-distearin.   The monostearin fraction was composed of indistinct crystals, m. p. 79—80°, hydroxyl number, 311·4.   H. W.

Chemistry of the Glutaconic Acids. XI. The Occurrence of 1 : 3-Addition to the Normal Form. JOCELYN FIELD THORPE (T., 1919, 115, 679—686).

Lactonic Acids. BROR HOLMBERG (*Svensk. Kem. Tidskr.*, 1918, 30, 190—205, 215—222; from *Chem. Zentr.*, 1919, i, 223—224).— In extension of his work on the Walden inversion, the author has investigated the stereochemical and kinetic behaviour of lactonic acids.   The hydrolysis of malic acid lactone has been examined from these points of view, and, since the behaviour of *β*-lactones differs in several respects from that of γ-lactones, the work has also been extended to paraconic acid.

r-Malic acid lactone, shining leaflets or thin plates, m. p. 64—65°, is prepared by the action of moist silver oxide on *r*-iodosuccinic acid; *d-malic acid lactone*, colourless syrup, $[\alpha]_D +41°$, in aqueous solution (2·5%), is similarly obtained from *l*-iodosuccinic acid.   The rate of hydrolysis was measured by dissolving the crude acid in water or dilute nitric acid of the desired concentration and estimating the amount of lactone in the solution by heating a measured portion until hydrolysis was complete and determining the increase in acidity by titration.   Autohydrolysis is a rather slow, unimolecular change; nitric acid somewhat increases the velocity of action.   In acid solution, *d*-malic acid lactone yields a mixture of *r*- and *l*-malic acids, whilst almost pure *d*-malic acid is formed in alkaline solution.

The formation of paraconic acid by elimination of bromine from salts of itabromopyrotartaric acid is a unimolecular change which is not reversible in dilute solution.   As acid salt and to a still greater extent as free acid, itabromopyrotartaric acid is only slowly converted into its lactone.   Silver salts catalyse the elimination of bromine in acid solution.   The formation of paraconic acid from itamalic acid is reversible.   Acid salts of itamalic acid are only slowly converted into paraconic acid, and this is also true of the reverse action in neutral solution.   Lactone formation and hydrolysis are catalysed by hydrogen ions.   The affinity constants of itamalic acid and paraconic acid are approximately $K = 0·0003 -$ 0·0004.   The hydrolysis of paraconic acid by alkali is a bimolecular reaction.   H. W.

Action of Carbon Disulphide on Nitromethane. ERICH FREUND (*Ber.*, 1919, 52, [*B*], 542—544).—A mixture of nitromethane and carbon disulphide reacts with alcoholic potassium

hydroxide to give *potassium nitrodithioacetate*, as a brown, crystal-line precipitate, decomp. 203·5°. When heated with potassium hydroxide, it yields potassium nitroacetate (Steinkopf, A., 1909, i, 559), and its solutions do not give an acid reaction until one equivalent of acid has been added, this change being interpreted as follows:

$$OK·NO!CH·CS·SK \longrightarrow OH·NO!CH·CS·SK \longrightarrow NO_2·CH_2·CS·SK.$$
$$J.\ C.\ W.$$
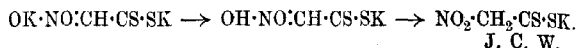
Some Metallic Derivatives of Ethyl Thioglycollate. CHARLES A. ROUILLER (*J. Amer. Chem. Soc.*, 1919, **41**, 777—781). —Ethyl thioglycollate was shown by Rowntree and Abel (*J.♦Phar-macol.*, 1910, **2**, 108) to dissolve antimonious and mercuric oxides, the hydrogen♦of the mercaptan group being completely replaced by the metal. The antimony derivative of the ester is an insoluble oil, but the corresponding amide is soluble in water and possesses trypanocidal properties. The author has found that the oxides of bismuth, copper, mercury, silver, zinc, tin, and arsenic react ener-getically with ethyl thioglycollate. It was hoped to prepare bactericidal substances, which would either be soluble in water or could be used in powder form on wound surfaces. *Triethyl bismuthtrithioglycollate*, Bi(S·CH₂·CO₂Et)₃, forms small, yellow crystals, m. p. 87—88°, soluble in alcohol. *Diethyl mercuri-dithioglycollate*, Hg(S·CH₂·CO₂Et)₂, long needles, m. p. 55°, is identical with the product obtained from mercuric chloride and two molecules of ethyl thioglycollate (Wislicenus, *Annalen*, 1868, **146**, 148). Ethyl silverthioglycollate, yellow needles from acetone, m. p. 75—77°, is with difficulty decomposed by concentrated nitric acid in sealed tubes. The action of silver nitrate on the ester was also investigated. With cupric hydroxide a crystalline substance is obtained which contains less than half the amount of copper to be expected from analogy with the previous reactions. It is very resistant to concentrated nitric acid at 200—270°.   F. C.

Constitution of Maltose. A New Example of Degradation in the Sugar Group. JAMES COLQUHOUN IRVINE and JAMES SCOTT DICK (T., 1919, **115**, 593—602).

Inversion of Sucrose by Mechanical Ionisation of Water. J. E. ABELOUS and J. ALOY (*Compt. rend.*, 1919, **168**, 1125—1128).—If 100 c.c. of a 5% solution of sucrose are passed five times through a Richardson pulveriser, 0·06 gram of invert sugar is obtained. The addition of sodium or potassium chloride appre-ciably increases the yield of invert sugar. Using a mixture of electrolytes such as is found in the Ringer-Locke solution, a slightly greater increase is obtained, and if a trace of zinc sulphate or, better still, a trace of zinc sulphate and a trace of manganese sulphate is added, the increase is still greater. On the other hand, the presence of a trace of potassium cyanide or of hydrocyanic

acid or of silver nitrate prevents the inversion taking place. The inversion is greater in Raulin's solution than in Locke's solution, and the authors have determined the effect of removing in turn each one of the ingredients of Raulin's solution in the inversion. The results so obtained are in agreement with those obtained by Raulin in his work on *Aspergillus niger*. Similarly, the antiseptics which inhibited the development of *Aspergillus niger* equally checked the inversion of sucrose. The curve showing the relationship between the amount of sucrose inverted and the number of passages through the pulveriser is sinusoidal, but slightly irregular. . W. G.

The Composition of Starch. I. Precipitation by Colloidal Iron. II. Precipitation by Iodine and Electrolytes. JOHN MELLANBY (*Biochem. J.*, 1919, **13**, 28—36).—When colloidal iron is added to a solution of starch three well-marked phases may be recognised; (i) a portion of the starch is precipitated by the colloidal iron only, (ii) a second portion of the starch is carried down with the colloidal iron when an electrolyte is added, and (iii) the filtrate from (ii) contains unprecipitated starch. Eighty % of the starch is precipitated in the first phase, independently of the amount of iron added. Starch in solution bears a negative charge. From these observations it is concluded that amylogranulose may be divided into three fractions, α, β, and γ, according to their precipitability by colloidal iron.

Quantitative studies of the reaction between starch and iodine indicate that a quantitative reaction takes place between the starch and the ionised iodine. The theory that iodine reacts chemically with starch is strengthened by the fact that the equivalent point is not affected by dilution, temperature, or the precipitating electrolyte. On this basis the least value for n for $(C_6H_{10}O_5)_n$ is 10, assuming that one molecule of starch reacts with one atom of iodine. This value is, of course, only a mean value for a number of starch complexes, such as α, β, and γ granulose, in which n is continually varying. For amylogranulose γ (unprecipitated by colloidal iron), $(C_6H_{10}O_5)_5$ is equivalent to I. After the formation of the starch iodide it may adsorb further quantities of iodine, depending on the iodine concentration of the original mixture. J. C. D.

The Supposed Degradation of Starch by Formaldehyde. MARTIN JACOBY (*Ber.*, 1919, **52**, [*B*], 558—562).—Woker's assumption that formaldehyde resembles diastase in its action on starch is primarily based on the fact that mixtures of starch and formaldehyde soon lose the power of giving a blue colour with iodine (A., 1917, i, 61, 447). It is now shown that the addition of ammonium acetate is quite sufficient to restore this power, whereas it has no influence on the iodine reaction with starch which has been left with diastase (compare also von Kaufmann, *ibid.*, 251). J. C. W.

The Nature of Solutions of Starch in Formalin, and the Quantitative Re-conversion of Formalin-Starch into Starch. The Colour of Iodine Solutions. W. VON KAUFMANN and A. LEWITE (*Ber.*, 1919, **52**, [*B*], 616—627. Compare A., 1917, i, 251).—The fact that solutions of starch and formalin merely contain an additive compound of the two agents and not hydrolytic products as Woker supposed, is proved by the quantitative recovery of absolutely unchanged starch from such mixtures by precipitation with alcohol.

The colorations with iodine which such solutions produce (resembling those given by partly hydrolysed starch) may be explained in the terms of colloid chemistry. If, as Harrison assumes (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 5), the well-known blue colour is the colour of colloidal iodine protected by the starch, then formaldehyde causes a reversible increase in the degree of dispersion, and the addition of electrolytes an aggregation of the particles (the blue colour is restored by electrolytes), which is furthermore hindered by the addition of a protective colloid like gum-arabic.

The colour of iodine solutions in halogen derivatives of methane and ethane changes from brown to violet according as the number of un-substituted hydrogen atoms falls.   ♣   J. C. W.

Space Representation of Organic Nitrogen Compounds. PANCHANAN NEOGI (*J. Amer. Chem. Soc.*, 1919, **41**, 622—639).— A theoretical paper, in which it is shown that the properties of nitrogen compounds can only be explained on the assumption of a tetrahedral formula for nitrogen, using the complete figure for quinquevalent nitrogen (I) and the "inner tetrahedron" for tervalent nitrogen (II), thus:

Amine (in-tetrahedron)   Amine Oxide   Ammonium Compound
(II.)   (III.)   (I.)
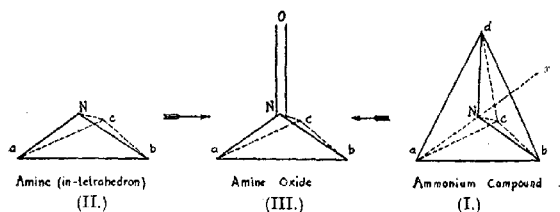
The subjects discussed are as follows. (1) The non-equivalence of the fifth bond, as revealed by the discovery of isomerides of the type $(NMe_3 \cdot OR)OR'$ and $(NMe_3 \cdot OR')OR$ (Meisenheimer, A., 1913, i, 595). (2) The non-existence of any isomerides of the types Na_3bx and Na_2bcx, and the existence of only two optical isomerides of the type $Nabcdx$. (3) The existence of only four optical isomerides in the case of compounds containing one asymmetric carbon

and one asymmetric nitrogen, or two asymmetric nitrogen atoms. (4) The non-existence of isomeric pyridinium and quinolinium compounds and the existence of isomeric tetrahydroquinolinium salts. (5) The failure to resolve amines of the type Nabc into optical isomerides has hindered the general acceptance of a space representation for tervalent nitrogen, although the above formula is used to explain the isomerism of the oximes, etc. It also explains why $tert$.-amines of this type give enantiomorphous amine-oxides on oxidation (Meisenheimer, A., 1912, i, 25), these compounds being represented as in (III) above.   J. C. W.

Preparation of Diacetonamine. ARTHUR ERNEST EVEREST (T., 1919, 115, 588—592).

The Mechanism of the Artificial Formation of Carbamide by Oxidation, and the Synthesis of the Natural Principals in Plants. R. FOSSE ($Compt. rend.$, 1919, 168, 1164—1166. Compare this vol., i, 297).—The oxidation of very small amounts of dextrose in strong ammonium hydroxide solution gives rise to considerable proportions of cyanic acid and carbamide. After tautomerisation of the ammonium cyanate by heat the yield of carbamide exceeds 70% of the dextrose used. Much higher yields of carbamide are obtained by oxidising, under the same experimental conditions, formaldehyde or urotropine. The author suggests that in the formation of carbamide from sugars by oxidation, formaldehyde is first formed, and is then converted by the action of ammonia and oxygen into hydrogen cyanide, which is further oxidised to cyanic acid, which with ammonia yields carbamide.   W. G.

Certain Metallo - Ferrocyanide Compounds, their Behaviour towards Chlorine and Bromine, and their Use in Analysis. FRANZ FELIX WERNER ($Zeitsch. anal. Chem.$, 1919, 58, 23—24. Compare A., 1912, ii, 687).—$Manganese ferrocyanide.$ —A white substance which is coloured green by chlorine water and oxidised to the brown ferricyanide by bromine water. $Nickel ferrocyanide.$—Bluish-green; not attacked by chlorine water, but converted into the brown ferricyanide by bromine water. $Cobalt ferrocyanide.$—An unstable, green compound, which chlorine water oxidises to the ferricyanide; it is decomposed by bromine water, yielding black, hydrated cobalt oxide. $Mercurous ferrocyanide.$— The grey compound is coloured green when treated with chlorine water or bromine water. $Mercuric ferrocyanide.$—White; chlorine water colours it green and bromine water brown. $Bismuth ferrocyanide.$—A yellowish-green compound which is not attacked by chlorine water or bromine water. [See further, $J. Soc. Chem. Ind.$, 1919, July.]   W. P. S.

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The Benzene Problem. A. VON WEINBERG (*Ber.*, 1919, **52**, [*B*], 928—940).—A theoretical paper, in which the author advances an explanation of the atomic structure of benzene based on the continuous oscillation of the atoms within the molecule. The author considers that in the case of the double bond two valencies of one atom saturate or strive to saturate two valencies of a neighbouring atom in consequence of the oscillation of the atomic nuclei; a considerable amount of evidence in favour of this hypothesis is deduced from consideration of the internal energy, molecular volume, absorption spectra, intramolecular change, and Walden inversion of substances containing unsaturated groups and of the influence of double bonds on the stability of the molecule. The argument is extended to conjugated linkings and thence to benzene; in the latter case the six carbon atoms only lie in one plane as a transitory phase; otherwise, the atoms 1, 3, 5 and the atoms 2, 4, and 6 are on opposite sides of the plane. The oscillation model is shown to account satisfactorily for the phenomena of substitution and to allow the construction of symmetrical formulæ for naphthalene, anthracene, phenanthrene, and pyrene, whilst it also accounts for the difference in properties between benzene and *cyclo*octatetraene; it leads to a uniform formulation of *p*-quinones and quinols, and accounts for the existence of two forms of *o*-quinones. Triphenylmethyl and the metallic ketyls can be formulated without recourse to tervalent carbon, whilst the phenomena of hydrogenation of the phthalic acids are also explained. For details, the original paper must be consulted. H. W.

The Melting Points, Refractive Indices and Densities of a Series of Dihalogenobenzenes. J. NARBUTT (*Ber.*, 1919, **52**, [*B*], 1028—1034).—The melting points were determined by observation of the cooling curves of the molten substances, and are accurate to within $\pm 0\cdot 02°$ for m. p.'s above the atmospheric temperature and to within $\pm 0\cdot 1°$ for those of lower temperature; the error in the case of the refractive indices, determined with an Abbé refractometer, does not exceed $\pm 0\cdot 0002$–3, whilst the densities are accurate to $\pm 0\cdot 0001$–2. The following constants have been determined : *p*-dichlorobenzene, m. p. $52\cdot 9°$; *o*-dichlorobenzene, m. p. $-17\cdot 5°$, D_4^{15} $1\cdot 3104$, $D_4^{20\cdot 4}$ $1\cdot 3048$, n_D^{15} $1\cdot 5524$; *m*-dichlorobenzene, m. p. $-24\cdot 4°$, D_4^{15} $1\cdot 2937$, D_4^{20} $1\cdot 2881$, $n_D^{15\cdot 3}$ $1\cdot 5472$; *p*-chlorobromobenzene, m. p. $64\cdot 6°$; *o*-chlorobromobenzene, m. p. $-12\cdot 6°$, D_4^{15} $1\cdot 6511$, D_4^{20} $1\cdot 6444$, $n_D^{17\cdot 3}$ $1\cdot 5821$; *m*-chlorobromobenzene, m. p. $-21\cdot 2°$, D_4^{15} $1\cdot 6365$, D_4^{20} $1\cdot 6297$, $n_D^{17\cdot 1}$ $1\cdot 5773$; *p*-dibromobenzene, m. p. $86\cdot 9°$; *o*-dibromobenzene, m. p. $+1\cdot 8°$, D_4^{15} $1\cdot 9633$, D_4^{20} $1\cdot 9557$, $n_D^{17\cdot 4}$ $1\cdot 6117$; *m*-dibromobenzene, m. p. $-6\cdot 9°$, D_4^{15} $1\cdot 9599$, D_4^{20} $1\cdot 9523$, $n_D^{17\cdot 4}$ $1\cdot 6083$; *p*-bromoiodobenzene, m. p. $90\cdot 1°$; *o*-bromoiodobenzene, m. p. $+2\cdot 1°$; *m*-bromoiodobenzene, m. p. $-9\cdot 3°$; *p*-di-iodobenzene, m. p. $129\cdot 0°$; *o*-di-iodobenzene, m. p. $23\cdot 4°$; *m*-di-iodobenzene, m. p. $34\cdot 2°$. H. W.

Products of Nitration of *p*-Cymene. OSSIAN ASCHAN [with TERÄSVUORI and PER EKWALL] (*Finska Kem. Medd.*, 1918, 5 pp.; from *Chem. Zentr.*, 1919, i, 227).—Direct nitration of cymene

yielded 2-nitrocymene, D_4^{20} 1·067, in minimal amount. Cymene was also gradually added to well-cooled concentrated nitric acid (D 1·52), and the following substances were isolated by prolonged fractional crystallisation of the solidified product. I. *Substance*, $C_{18}H_{17}O_{10}N_5$, yellow needles, m. p. 70°, which when reduced with ammonium sulphide yielded an *amine*, orange needles, m. p. 77—78° (*hydrochloride*, m. p. 215—218°). II. 3:5-*Dinitro-p-cymene*, greenish-white plates, m. p. 54°, which were reduced to *nitro-carvacrylamine*, yellow needles or prisms, m. p. 80—82° (*hydrochloride*, pale red crystals, m. p. 208—210°; *acetyl* derivative, m. p. 111°). *Nitrocarvacrol*, needles, m. p. 116—117°, was formed as by-product during diazotisation. III. *Substance*, $C_{10}H_{12}O_5N_2$, probably dinitrohydroxy-*p*-cymene, $C_6H_2Me(NO_2)_2 \cdot CMe_2 \cdot OH$, prisms or plates, m. p. 90—91°.   H. W.

The Dimethylnaphthalenes of Coal Tar. R. WEISSGERBER and O. KRUBER (*Ber.*, 1919, **52**, [*B*], 346—370).—Physical methods for the separation of the dimethylnaphthalenes in the heavy-oil fraction, b. p. 260—265°, seem to be out of the question, and when it is considered how many sulphonic acids could be formed by the ten possible isomerides, no great help could be expected from the sulphonation method which has served so well in the case of the polymethylbenzenes. Nevertheless, the authors have tried the method, and by varying the conditions have succeeded in isolating the 1:6-, 2:6-, and 2:7-isomerides with far less trouble than was anticipated.

1:6-DIMETHYLNAPHTHALENE.—The crude oil is purified by alternate fractionation and agitation with small quantities of concentrated sulphuric acid in the cold. It is then stirred with 60% of its weight of 98% sulphuric acid for eight to ten hours at about 40°, when the pasty mass of sulphonic acids is separated and mixed with a little water. A solid *sulphonic acid* is deposited, which is purified by crystallisation from 33% sulphuric acid and converted into its *sodium* salt, bundles of needles, 1H$_2$O, and *amide*, $C_{12}H_{13}O_2NS$, m. p. 185°. The sulphonic acid is hydrolysed by means of steam at 130—140° to 1:6-*dimethylnaphthalene*, which has b. p. 262—263°, D^{15} 1·0056 (α-methylnaphthalene has $D^{11·5}$ 1·0267), and forms a *picrate*, long, orange-red needles, m. p. 114°. The constitution of the hydrocarbon is revealed by the following series of reactions.

By the alkaline fusion of the sulphonate, 4:7-*dimethyl-α-naphthol* is obtained, in slender needles, m. p. 82°, which couples with benzenediazonium chloride to form a *dye*, $C_{18}H_{16}ON_2$, dark red leaflets, m. p. 134°, which is insoluble in, and indifferent to, potassium hydroxide, and is therefore an *o*-hydroxyazo-compound. On oxidation with chromic acid in glacial acetic acid, the hydrocarbon yields 2:5-*dimethyl-α-naphthaquinone*, which crystallises in pale yellow rosettes of pungent-smelling needles, m. p. 95°, and may be oxidised further, by permanganate, to 3-methyl-*o*-phthalic acid (Jürgens, A., 1907, i, 1036). The production of the *o*-azo-dye, the

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p-quinone, and the 3-methylphthalic acid indicates that the hydrocarbon is either a 1:6- or 1:7-dimethylnaphthalene and the sulphonic acid the 4-derivative. For the final decision, oxidation to a dicarboxylic acid is necessary, but many methods were tried before this could be accomplished. Oxidation with alkaline ferricyanide gives *naphthalene*-1:6-*dicarboxylic acid*, which crystallises in microscopic needles, m. p. 310°, and forms a *methyl* ester, rosettes of needles, m. p. 99°. Prolonged boiling with about 5% nitric acid, however, gives chiefly 6-*methyl-α-naphthoic acid*, which crystallises in slender, white needles, m. p. 150—152°, forms a *methyl* ester, a pale yellow oil with a resinous odour, b. p. 183—187°/30 mm., and an *ethyl* ester, b. p. 203—205°/30 mm., and yields β-methylnaphthalene when heated with hydrochloric acid at 222—230°.

The above dicarboxylic acid was also prepared as follows: β-Naphthylamine-5-sulphonic acid is diazotised and boiled with cuprous cyanide, the *potassium* 6-*cyanonaphthalene-1-sulphonate* is distilled with potassium cyanide, and the 1:6-dicyanonaphthalene (short needles, m. p. 208—210°; compare Darmstädter and Wichelhaus, *Annalen*, 1869, **152**, 309) is hydrolysed.

2:6-DIMETHYLNAPHTHALENE.—If the sulphonation is carried out at 135—140°, and the product is poured on ice, a much less soluble *sulphonic acid* soon crystallises. This crystallises in large, glistening leaflets, gives a sparingly soluble *sodium* salt, 5H₂O, and an *amide*, m. p. 265—266°, and yields the known 2:6-dimethylnaphthalene on hydrolysis. The hydrocarbon has m. p. 110—111°, b. p. 261—262°, and has the odour of aniseed, whereas the specimen obtained by Baeyer and Villiger from ionone (A., 1899, i, 922) had the odour of orange blossom. The identity of the compound is established, however, by its oxidation with chromic acid to 2:6-dimethylnaphtha-1:4-quinone and then by permanganate to trimellitic acid (*ibid*.).

The explanation of the different course of the sulphonation was found by sulphonating the pure hydrocarbons. 1:6-Dimethylnaphthalene yields the 4-sulphonic acid in the cold, but a mixture of freely soluble acids at above 100°; 2:6-dimethylnaphthalene yields the freely soluble 8-sulphonic acid in the cold, which is hydrolysed to the hydrocarbon by boiling with about 70% sulphuric acid, and converted into the 7-sulphonic acid by heating with 78% sulphuric acid at 135—140°. The constitution of the sulphonic acids follows from the properties of the corresponding naphthols. 2:6-*Dimethylnaphthalene-8-sulphonic acid* [3:7-*dimethyl-α-naphthalenesulphonic acid*] crystallises in flat needles and tablets, its *chloride* in stout prisms, m. p. 105—107°, and its *amide* in rosettes of leaflets, m. p. 207°. The product of the alkaline fusion, 3:7-*dimethyl-α-naphthol*, forms colourless needles, m. p. 105—106°, and couples with benzenediazonium chloride to give *bisbenzeneazo*-3:7-*dimethyl-α-naphthol*, C₂₄H₂₀ON₄, in steel-blue needles, m. p. 191°. 3:7-*Dimethyl-β-naphthalenesulphonic acid*, the above product of the sulphonation at 135—140°, gives rise to 3:7-*dimethyl-β-naphthol*, which crystallises in glistening needles, m. p. 173—174°,

and forms a *benzeneazo*-compound, in brilliant orange-red needles, m. p. 149—151°. This is converted into 3:7-*dimethylnaphtha-1:2-quinone*, ruby-red needles, m. p. 151—152°, by reduction to the aminonaphthol, followed by oxidation with dichromate. 2:6-Dimethylnaphtha-1:4-quinone (above) reacts with phenylhydrazine to form 4-*benzeneazo*-2:6-*dimethyl-α-naphthol*, which crystallises in fiery orange-red needles, m. p. 240—241° (decomp.), and changes in alcoholic solution from orange to magenta on the addition of alkali hydroxide.

2:7-DIMETHYLNAPHTHALENE.—For practical purposes, it is not advisable to isolate the 2:6-isomeride from the original oil, but to proceed as follows: the oil is sulphonated in the cold, and the liquid sulphonic acids removed from the solid 1:6-dimethylnaphthalenesulphonic acid are heated at 150—160° for a few hours and then hydrolysed, giving a mixture of solid and liquid hydrocarbons. The solid mixture generally has m. p. 50—60°, but is frequently so rich in the 2:6-isomeride as to yield this readily by fractional crystallisation. If not, it is sulphonated at 135—140°, the solid 2:6-dimethylnaphthalenesulphonic acid is removed, and the liquid acids hydrolysed again. Once more a mixture of solid hydrocarbons with low m. p. is obtained. This is then sulphonated at about 40°, and the pasty product crystallised from 30% sulphuric acid. Two sulphonic acids separate, which are hydrolysed in the usual way, when 2:7-*dimethylnaphthalene* is obtained in glistening leaflets with an aromatic odour, m. p. 96—97°, b. p. 262°, the *picrate* crystallising in pale yellow needles, m. p. 135—136°.

The constitution of the new hydrocarbon is established in the usual way. When sulphonated at 100°, it yields 2:7-*dimethylnaphthalene-3-sulphonic acid*, which crystallises in pearly, swordlike forms, and forms a *sodium* salt, bundles of needles, and an *amide*, m. p. 197—198°. The sodium salt can also be isolated from the above crude mixture obtained by sulphonating in the cold, or from the mother liquors of the above 2:6-dimethylnaphthalenesulphonate. When fused with potassium hydroxide, the salt yields 3:6-*dimethyl-β-naphthol*, in lanceolate crystals, m. p. 171—172°, which gives a brilliant orange-red *benzeneazo*-dye, m. p. 183—184°. When the dye is reduced and the white amine is oxidised by chromic acid, 3:6-*dimethylnaphtha*-1:2-*quinone* is obtained, in stout, brownish-red prisms, m. p. 152—153°. The isomeric 3:6-*dimethylnaphtha*-1:4-*quinone*, yellow needles, m. p. 114—115°, is obtained by oxidising the hydrocarbon with chromic acid, and it yields trimellitic acid on oxidation with permanganate.

The coal-tar fraction, b. p. 220—290°, is commonly regarded as being poor in solid ingredients, in fact, is often used to maintain other fractions in the liquid state. The discovery of two solid dimethylnaphthalenes is therefore contrary to this idea. The only genuine oils in the fraction are the β-methyl- and 1:6-dimethylnaphthalenes, the fluidity being due to the enormous depression of the freezing point mutually exerted by the ingredients. A

possible outlet for naphthalene as an oil would therefore consist in methylating it.   J. C. W.

2 : 3-Dimethylnaphthalene in Coal Tar. R. WEISSGERBER (*Ber.*, 1919, **52**, [*B*], 370—371).—On working up the liquid sulphonic acids accompanying the 2:6-dimethylnaphthalene-sulphonic acid (preceding abstract), a well-defined sodium salt was once accidentally obtained which gave a fourth dimethyl-naphthalene, crystallising in large leaflets, m. p. 104—105°. By direct comparison, this has now been identified with the 2:3-di-methylnaphthalene (guaiene) recently obtained by Schroeter and others from guaiacum resin (this vol., i, 84).   J. C. W.

Oximinoacetanilides and their Condensation to Isatins. T. SANDMEYER (*Helv. Chim. Acta*, 1919, **2**, 234—242).—If a freshly prepared solution of hydroxylamine sulphate is boiled with aniline or many of its derivatives and chloral hydrate, oximinoacet-anilides are formed, according to the equations: $CCl_3 \cdot CHO +$ $NH_2 \cdot OH \longrightarrow CCl_3 \cdot CH:N \cdot OH$; this
$$+ NH_2Ph + H_2O = NHPh \cdot CO \cdot CH:N \cdot OH.$$
The majority of these compounds, if the ortho-position is un-occupied, give excellent yields of isatins when heated with sulphuric acid at temperatures varying from 55° to 100° and then diluted with water; thus:
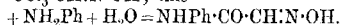
$$NHPh \cdot CO \cdot CH:N \cdot OH - H_2O \longrightarrow$$

$$C_6H_4 {<}^{NH-}_{C(:NH)}{>}CO \xrightarrow{+H_2O} C_6H_4 {<}^{-N}_{CO}{>}C \cdot OH.$$
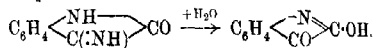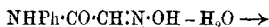
The solution of hydroxylamine sulphate is obtained by boiling one of hydroxylaminesulphonic acid, prepared by Raschig's method. The oximinoacetanilides are all more or less pale yellow, floccu-lent, crystalline precipitates. The following have been prepared: *oximinoacet-anilide*, m. p. 175°; -*o*-, -*m*-, and -*p*-*toluidides*, m. p.'s 121°, 146°, 162° respectively; -*m*- and -*p*-*xylidides*, m. p.'s 161° and 151°; -*o*-*anisidide*, m. p. 140°; -*p*-*phenetidide*, m. p. 195°; -*methyl*-, -*ethyl*-, and -*benzyl*-*anilides*, m. p.'s 145°, 160°, and 142°; -*o*-, -*m*-, and -*p*-*chloroanilides*, m. p.'s 150°, 154°, 165°; -2:5-, -3:4-, and -3:5-*dichloroanilides*, m. p.'s 163°, 158°, 185°; -5- and -4-*chloro-o*-*toluidides*, m. p.'s 167°, 148°; -6- and -4-*chloro*-m-*toluidides*, m. p.'s 187°, 134°; -2- and -3-*chloro-p-toluidides*, m. p.'s 177°, 188°; -4-*chloro-o-anisidide*, m. p. 182°; -*p*-*bromoanilide*, m. p. 167°; -2:4-*dibromoanilide*, m. p. 215°; and *oximinoacetanthranilic acid*, m. p. 208°.

  The following isatins are new: 4:7-*dimethylisatin*, orange-yellow, m. p. 250°; 7-*chloroisatin*, reddish-brown, m. p. 175°; 4:6-*dichloro-isatin*, lemon-yellow, m. p. 250°; 4-*chloro-7-methylisatin*, orange-yellow, m. p. 273°; 5-*chloro-7-methylisatin*, yellowish-brown, m. p. 265°; 7-*chloro-4-methylisatin*, orange-yellow, m. p. 252°; 4-*chloro-7-methoxyisatin*, dark red, m. p. 240°; and *isatin-7-carboxylic acid*, brownish-yellow, m. p. 235°.   J. C. W.

The Conception of Internal Molecular Strain and the Theory of Benzene. D. VORLÄNDER (*Ber.*, 1919, 52, [*B*], 263—283).—A theoretical paper dealing chiefly with the problems of orientation in the benzene series.

I. *Positive and Negative Radicles attached to the Benzene Nucleus.*—The various radicles are sharply divided into two classes, according to the position occupied by the second substituent in bromination, nitration, or sulphonation. One group exerts a *positive* influence, directing the new substituent into the *meta*-position, and includes $\cdot SO_3H$, $\cdot NO_2$, $\cdot CHO$, $\cdot CH \dot{.} NO_2H$, $\cdot CO_2H$, $\cdot CO_2Alk$, $\cdot CO \cdot NH_2$, $\cdot COAlk.$, $\cdot CO \cdot CO_2H$, $\dot{.}C \cdot OH$, $\cdot CN$, $\cdot CCl_3$, $\cdot N\overset{\cdot}{H}_3X$, $\cdot NH_2Alk.X$, $\cdot NHAlk._2X$, $\cdot NAlk._3X$, $\cdot NH_2AcylX$. The other group has a *negative* influence, and is *ortho-para* orienting; it includes halogens, $\cdot OH$, $\cdot OAlk$, $\cdot OAcyl$, $\cdot NH_2$, $\cdot NHAlk.$, $\cdot NAlk._2$, $\cdot NHAcyl$, $\cdot N\dot{.}\overset{\cdot}{N}\cdot$, $\cdot CH_3$, $\cdot CH_2Alk.$, $\cdot CHAlk._2$, $\cdot CMe_3$, $\cdot CH_2Cl$, $\cdot CH_2 \cdot O \cdot NO_2$, $\cdot CH_2 \cdot SO_3H$, $\cdot CH_2 \cdot NH_2$, $\cdot CH_2 \cdot CN$, $\cdot CH_2 \cdot CO_2H$, $\cdot CH_2 \cdot CH_2 \cdot CO_2H$, $\cdot CH \dot{.} CH \cdot CO_2H$, $\cdot CH \dot{.} CH \cdot NO_2$, $\cdot C \dot{.} C \cdot CO_2H$, $\cdot C_6H_5$. At first sight, it would seem to be a novel conception to regard the groups $\cdot SO_3H$, $\cdot CO_2H$, and $\cdot NR_3X$ as positive and $\cdot NH_2$ as negative, and to find a difference between $\cdot COMe$ on the one hand and $\cdot OMe$ and $\cdot CH_3$ on the other, but the author's notion is not based on any valency theories at all. The terms $+$ and $-$ are used to express the kind of antithesis or strain between the connected atoms. Thus, in any member of the above positive series, the atom which is attached to the benzene ring is positive; for example, $Ph \cdot \overset{+}{N}R_3 \cdot \overset{-+}{O}H$, $Ph \cdot \overset{+-}{N}O_2$, $Ph \cdot \overset{+-}{C}OR$, $Ph \cdot \overset{+}{S}O_2 \cdot \overset{-+}{O}H$, $Ph \cdot \overset{+}{C}O \cdot \overset{-+}{O}H$. In the negative series, the connecting atom is negative, thus: $Ph \cdot \overset{-}{O}CH_3$, $Ph \cdot \overset{-+}{C}H_3$, $Ph \cdot \overset{-}{N}H_2$, $Ph \cdot \overset{-}{O}H$.

II. *The Nature of the Ammonium Salt Group,* $\cdot NR_3X$.—In the following abstract it is shown that aromatic quaternary ammonium salts are difficult to brominate or nitrate, but that the second substituent goes to the *meta*-position. The group $\cdot NR_3X$ therefore resembles the $\cdot NO_2$ group. This is interesting in view of the fact that anilines and their alkyl and acyl derivatives, which give *ortho-* and *para-*derivatives when brominated or nitrated in acetic acid solution, yield meta-compounds if dissolved in an excess of concentrated sulphuric acid, for then they are acting as ammonium salts. Like the $\cdot CO$, $\cdot NO_2$, and $\cdot CN$ groups, also, the $\cdot NR_3X$ group protects the benzene nucleus against oxidation and coupling; for example, when *o*-tolyltrimethylammonium sulphate is oxidised, it merely gives *o*-benzobetaine (this vol., i, 262). Unlike these groups, however, the $\cdot NR_3X$ radicle has no chromophoric properties, in spite of the fact that the production of perbromides, etc., shows it to be somewhat unsaturated.

III. *Nitration of Benzotrichloride and* tert.-*Butylbenzene.*— Under conditions which preclude the hydrolysis of benzotrichloride, nitration gives a meta-compound (this vol., i, 263). This illustrates the difference between the $\cdot CH_3$ group, in which the

carbon is $-$, and the $\cdot CCl_3$ group, in which it is $+$. *tert.*-Butyl-benzene, on the other hand, gives almost entirely a *p*-nitro-deriv-ative (this vol., i, 261). It is very difficult to chlorinate or oxidise, there being apparently a steric hindrance against the occupation of the ortho-position.

IV. *The Benzene Theory* (compare A., 1902, ii, 250).—The carbon atoms in the benzene ring are also written alternately $+$ and $-$. If the ring bears a positive substituent like $\cdot NO_2$, the formula may be expressed as in (I), if a negative substituent like $\cdot NH_2$, as in (II), in which the strong lines represent greater, and the weak lines lesser, tensions.

(I.)   (II.)
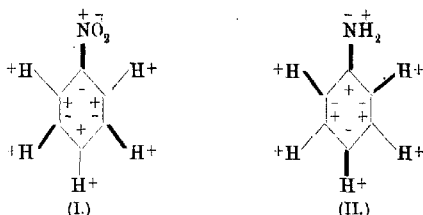
This conception helps to explain why compounds of the first type are more stable than the others, and why the first give meta-derivatives with halogen or nitric and sulphuric acids, whilst the second give ortho- and para-compounds. Other problems are dis-cussed along the same lines, including the position occupied by a third substituent when (*a*) two positive, (*b*) two negative, and (*c*) one positive and one negative substituents are already present.

J. C. W.

Bromination and Nitration of Aromatic Quaternary Ammonium Salts. D. VORLÄNDER and ERNST SIEBERT (*Ber.*, 1919, **52**, [*B*], 283—307).—I. *Bromination of Phenyltrimethyl-ammonium Bromide.*—This salt is prepared as follows: dimethyl-aniline is warmed with methyl sulphate and benzene, the hygro-scopic product, $NMe_3Ph\cdot SO_4Me$, m. p. 71—92° (Ullmann, A., 1903, i, 394), is dissolved in 20% hydrobromic acid and treated with bromine, and the tribromide so formed (Tafel, A., 1898, i, 519) is boiled with water and the solution evaporated. Phenyltrimethyl-ammonium bromide forms colourless crystals, m. p. 214°, and the corresponding picrate has m. p. 115°. Tafel did not succeed in brominating the salt (A., 1898, i, 471), but it is now found that reaction with bromine takes place at 70° in the presence of iron powder, the product being m-*bromophenyltrimethylammonium bromide*, $C_6H_4Br\cdot NMe_3Br$. This crystallises in stout prisms, m. p. 236—238° (decomp.), combines with bromine to form an orange-red *tribromide*, m. p. 93—95°, and a yellow *dibromide*, m. p. 120—122°, and may be converted into the corresponding iodide, colourless prisms, m. p. 202° (Wurster and Scheibe, A., 1879,

107), *tri-iodide*, dark brown leaflets, m. p. 110°, and yellow *picrate*, m. p. 151°. The iodide decomposes at 165°/13 mm. into *m*-bromodimethylaniline (*ibid.*), which has m. p. 9—10°, b. p. 125°/10 mm., 253—254°/atm., and is characterised by its *picrate*, hexagonal tablets or prisms, m. p. 134—138°, and by conversion into *m*-bromo·*p*-nitrosodimethylaniline, brownish-green needles, m. p. 116° (not 148° as given by Wurster and Scheibe).

If the bromination is carried out at 100—120°, the product is 3:4-*dibromophenyltrimethylammonium bromide*, which crystallises as a mass of minute filaments, m. p. 180° (decomp.). The corresponding *tribromide*, $C_6H_3Br_2\cdot NMe_3\cdot Br_3$, forms golden-yellow leaflets, m. p. 147—149° (decomp.); the *iodide* crystallises in almost white, glistening needles, m. p. 185° (decomp.), and the *tri-iodide* forms brown leaflets, m. p. 136—138°. If the iodide is converted into the hydroxide, and this is distilled under reduced pressure, 3:4-*dibromodimethylaniline* is formed. This crystallises in needles or hexagonal tablets, m. p. 68—70°, decomposes into a reddish-violet dye on distillation under ordinary pressures, and may also be obtained by brominating 3-bromodimethylaniline or methylating 3:4-dibromoaniline. The base forms a characteristic *picrate*, flat, yellow needles, m. p. 142—146°, and a *perbromide*, m. p. 161—163° (decomp.), yields a mixture of products when treated with nitrous acid, including a golden-yellow *nitro*-compound, m. p. 131°, and may be converted into the above 3:4-dibromophenyltrimethylammonium salts after treatment with methyl sulphate.

For the sake of comparison, the unknown 3:5- and 3:6-dibromodimethylanilines have been prepared from the corresponding anilines by means of methyl sulphate. 3:5-*Dibromodimethylaniline* crystallises in large, white tablets, m. p. 77—79°, and forms a *picrate*, m. p. 151—153°, and 3:5-*dibromophenyltrimethylammonium tribromide* may be precipitated by means of bromine and hydrobromic acid from the alkaline mother liquor obtained in the preparation as yellow leaflets, m. p. 149° (decomp.). 3:6-*Dibromodimethylaniline* has m. p. below –35°, b. p. 134—137°/10 mm., forms a pale yellow *picrate*, m. p. 149°, and reacts with nitrous acid to give 3:6-*dibromonitrosomethylaniline*,

$$C_6H_3Br_2\cdot NMe\cdot NO,$$
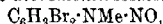
in small, white needles, m. p. 86—87°. 3:6-*Dibromophenyltrimethylammonium tribromide* forms golden-yellow leaflets, m. p. 135—136° (decomp.).

II. *Nitration of Phenyltrimethylammonium Nitrate.*—The bromide is converted into the nitrate, m. p. 110—115°, by evaporating two or three times with dilute nitric acid. Nitration takes place when the salt is heated at 100° with fuming nitric acid for eight hours, the product being *m*-nitrophenyltrimethylammonium nitrate, which crystallises in colourless prisms, m. p. 220—240° (decomp.) (compare Tafel, *loc. cit.*). The corresponding *picrate* forms yellow tablets, m. p. 151—153°, the *iodide* hexagonal or quadratic tablets, decomp. 205°, and the *tri-iodide* dark brown

leaflets, m. p. 143—145° (decomp.). The iodide yields m-nitro-dimethylaniline, m. p. 58—60°, when heated in a vacuum, the product being identical with one made by Ullmann's method (A., 1900, i, 619). The action of sodium nitrite on hydrochloric acid solutions of this base leads to different products, according to the concentration of the acid. In dilute acid, the product is m-nitro-nitrosomethylaniline, $NO_2 \cdot C_6H_4 \cdot NMe \cdot NO$, m. p. 76° (Noelting and Stricker, A., 1886, 544); from more concentrated solutions (acid with D 1·1—1·2), the products also include 3:4- and 3:6-dinitro-dimethylanilines, m. p.'s 174—175° and 112° respectively.

III. *Nitration of* o-*Tolyltrimethylammonium Nitrate*.—Di-methyl-o-toluidine is methylated by means of methyl sulphate, the product is converted into the ammonium tribromide, and this is heated with dilute nitric acid. o-*Tolyltrimethylammonium nitrate* crystallises in quadratic leaflets, m. p. 175°; the corresponding *picrate* has m. p. 112—114°, the *mercurichloride* m. p. 192° (decomp.), and the *aurichloride* m. p. 189°. The nitrate readily reacts with boiling nitric acid (D 1·51) to form 5-*nitro*-o-*tolyltri-methylammonium nitrate*, $NO_2 \cdot C_6H_3Me \cdot NMe_3 \cdot NO_3$, in flat needles, m. p. 230—235° (decomp.), which behave in a remarkable manner towards alkalis. When covered with 33% potassium hydroxide, the salt becomes bluish-green and then deep indigo-blue, changing to a reddish-violet solution on dilution, which gradually deposits brownish-red or green flocks. The corresponding *picrate* forms long, yellow needles, m. p. 202°, the *mercurichloride* long, white needles, m. p. 226° (decomp.), the *aurichloride* yellow leaflets, m. p. 200° (decomp.), the *platinichloride* orange-red needles and prisms, m. p. 233° (decomp.), and the *iodide* golden-yellow needles, m. p. 195° (decomp.). The iodide decomposes when heated in a vacuum into 4-nitrodimethyl-o-toluidine, $NO_2 \cdot C_6H_3Me \cdot NMe_2$, m. p. 13·5—15°, b. p. 160°/16 mm.; hydrochloride, m. p. 197° (decomp.) (compare Gnehm and Blumer, A., 1899, i, 266). When the ammonium hydroxide is evaporated in a flask and then heated, trimethylamine, formaldehyde, and other gases are evolved, and at 170—180°/15—30 mm., m-nitrodimethylaniline distils into the receiver.

IV. *Nitration of* m-*Tolyltrimethylammonium Nitrate*.—m-Tolu-idine is converted in the above manner into m-*tolyltrimethyl-ammonium nitrate*, which forms prismatic crystals, m. p. 134°, the corresponding *picrate* having m. p. 108°. When boiled with fuming nitric acid, the salt yields 4-*nitro*-m-*tolyltrimethyl-ammonium nitrate*, white tablets, m. p. 195° (decomp.), the corre-sponding *picrate* having m. p. 205°, the *iodide*, m. p. 165° (decomp.), and the *tri-iodide*, crystallising in violet-brown needles, m. p. 140°. The iodide decomposes at 210°/11 mm. into 6-nitro-dimethyl-m-toluidine, which crystallises in dark yellow, flat, tri-clinic needles, m. p. 83°. This has been prepared also by methyl-ating 6-nitro-m-toluidine (made from m-toluidine or m-cresol), and it corresponds with a nitrodimethyl-m-toluidine described by Wurster and Riedel (A., 1880, 109).

V. *Nitration of* p-*Tolyltrimethylammonium Nitrate.*—Dimethyl-*p*-toluidine is converted into p-*tolyltrimethylammonium tribromide*, golden-yellow leaflets, m. p. 113—115°, and then into the *nitrate*, white leaflets, m. p. 125°, and *picrate*, long, yellow needles, m. p. 195—197°, by the usual means. 3-*Nitro*-p-*tolylammonium nitrate* crystallises in glistening, white scales, m. p. 205—220° (decomp.), the *picrate* in long, yellow needles, m. p. 203°, the *tribromide* in long, yellow prisms, m. p. 152° (decomp.), the *iodide* in pale yellow prisms, m. p. 195° (decomp.), the *tri-iodide* in violet-brown prisms, m. p. 126°, and the *platinichloride* forms orange-yellow crystals, m. p. 207° (decomp.), and the *mercurichloride* long, white, prismatic needles, m. p. 141°. The iodide decomposes at 160°/12 mm. into 2-nitrodimethyl-*p*-toluidine, yellowish-red plates, m. p. 38°, the *picrate* having m. p. 147°. The base reacts with nitrous acid to form 2-nitrosonitrosomethyl-*p*-toluidine, m. p. 57—59° (Pinnow, A., 1896, i, 161), and it may be obtained by methylating 2-nitro-*p*-toluidine or nitrating dimethyl-*p*-toluidine (Haibach, A., 1902, i, 444; D.R.-P. 69188).   J. C. W.

Oxidation of Secondary and Tertiary Aromatic Amines. XX. Ditertiary Hydrazines and Related Substances. HEINRICH WIELAND (*Ber.*, 1919, **52**, [*B*], 886—893).—Although the explanation of the mechanism of the blue colour reaction of diphenylamine advanced by Kehrmann and Micewicz (A., 1912, i, 1020), and Wieland (A., 1913, i, 1386), has been generally accepted, certain details have been criticised by Marqueyrol and Muraour (A., 1914, i, 577). Thus, the removal of the imino-hydrogen atom by oxidation of the free base has been attributed by Wieland to the unsaturated nature of tervalent nitrogen; when this becomes saturated, as by salt formation, the oxidising agent appears to attack the benzene nucleus. Under similar conditions, however, the French chemists found diphenylamine to be apparently less readily oxidised in concentrated than in dilute acid solution; this is now shown to be due, however, to the consumption of the oxidising agent by side-reactions caused by the concentrated acid.

Diphenylmethylamine is readily oxidised to a carmine-red dye, which is reduced to NN′-*diphenyl*-NN′-*dimethylbenzidine*, colourless, silky needles, m. p. 171°. *Diphenylmethylaminesulphonic acid* is formed as a by-product of the methylation of diphenylamine with methyl sulphate; the *sodium* salt was analysed. The mechanism of the oxidation of salts of tertiary amines is also discussed, and it is suggested that the first stage of the process consists in the removal of the hydrogen atoms introduced with the acid, and that this is followed by oxidation of the *para*-hydrogen atoms; the first phase is then analogous to the formation of dianthrone from anthranol. The explanation is not, however, valid for triphenylamine, for which the primary addition of oxygen or hydroxyl is assumed.   H. W.

Ditertiary Hydrazines. XXI. Chlorotriarylmethanes and Diarylamines. HEINRICH WIELAND, BORIS DOLGOW, and TALBOT J. ALBERT (*Ber.*, 1919, **52**, [*B*], 893—898).—It has been previously shown that the dissociation products of ditertiary hydrazines unite with triphenylmethyl to yield triphenylmethyldiarylamines; attempts are now described to obtain these substances by the action of chlorotriphenylmethane on diarylamines. In general, however, derivatives of tetraphenylmethane are obtained, the formation of which is due to the transformation of the triarylmethyldiarylamines under the experimental conditions adopted: $CPh_3 \cdot NPh_2 \longrightarrow CPh_3 \cdot C_6H_4 \cdot NHPh$.

p-*Anilinotetraphenylmethane*, slender needles, m. p. 242°, after previous softening, is prepared by heating triphenylmethyl chloride and diphenylamine in benzene solution; it is oxidised by chromic acid in glacial acetic acid solution to a benzidine dye, and yields a *tribromo*-derivative, m. p. 214—215°. It can also be prepared by heating *N*-triphenylmethyldiphenylamine with diphenylamine hydrochloride in the presence of benzene, or by protracted heating of the first-named substance in glacial acetic acid solution. The action of chlorotriphenylmethane on *p*-ditolylamine, or the transformation of *N*-triphenylmethylditolylamine, leads to the formation of a *substance*, m. p. 217—218°, which probably has the constitution $CHPh_2 \cdot C_6H_4 \cdot N(C_6H_4Me)_2$. A similarly constituted compound, slender, colourless needles, m. p. 197—199°, is obtained from chlorotriphenylmethane and *p*-dianisylamine. Reaction between *p*-tetramethyldiaminodiphenylamine and chlorotriphenylmethane is of particular interest, since, in this instance, the primary product can be isolated, and is identical in all respects with that obtained from triphenylmethyl and the radicle $N(C_6H_4 \cdot NMe_2)_2$ (Wieland, A., 1915, i, 848); as by-product, the additive *compound*,

$$CPh_3 \cdot NCl \cdot C_6H_4Me_2 \cdot NH \cdot C_6H_4 \cdot NMe_2,$$
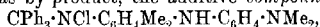
is formed, which decomposes into indamine and triphenylmethane.

H. W.

The Nitro-derivatives of Phenyl-β-naphthylamine. HUGH RYAN and JAMES J. DRUMM (*Proc. Roy. Irish Acad.*, 1918, **34**, [*B*], (8), 165—174).—Amongst the compounds proposed for use as stabilisers for nitrocellulose powders is phenylaceto-β-naphthalide. The nature of its action has not hitherto been investigated. Since it seemed likely that the stabilising action is due to its power of combining with nitrous and nitric acids, its reaction with these substances was examined.

Nitrogen peroxide, from lead nitrate, has apparently no action on phenylaceto-β-naphthalide in dry ethereal solution. In presence of moist ether, hydrolysis and nitration occur. Phenyl-β-naphthylamine and a mononitrophenyl-β-naphthylamine, colourless, cubical crystals from xylene, m. p. 119—120°, are formed. The orientation of the mononitro-derivative was not determined. It was also obtained from the stabiliser and cold concentrated nitric acid.

In alcoholic solution, the stabiliser slowly forms two trinitro-compounds, m. p. 242° and 179° respectively. The same compounds are produced when a mixture of amyl nitrite, nitric acid (1—6 molecules), and the stabiliser in glacial acetic acid is allowed to remain. Under similar conditions, in the absence of amyl nitrite, no action occurs. The trinitro-compound, m. p. 179°, is also obtained when phenyl-β-naphthylamine in glacial acetic acid is treated with a large excess of nitric acid. It forms orange crystals from glacial acetic acid. The yellow trinitro-compound, m. p. 242°, is also formed when phenyl-β-naphthylnitrosoamine reacts with nitric acid in glacial acetic acid, and is identical with 2′:4′-dinitrophenyl-1-nitro-2-naphthylamine, which was prepared by Goldberg's method (A., 1908, i, 288) from chloro-2:4-dinitrobenzene and 1-nitro-2-naphthylamine.

The authors have also prepared the following substances by the Goldberg reaction in hot nitrobenzene:

p-*Nitrophenyl-β-naphthylamine* (from β-naphthylamine and *p*-bromonitrobenzene) forms yellow, matted, acicular crystals from benzene, m. p. 283—284°, which give a bluish-violet coloration with concentrated sulphuric acid.

Phenyl-1-nitro-β-naphthylamine (from bromobenzene and 1-nitro-β-naphthylamine) forms deep red prisms from alcohol, m. p. 105—106°. Its solution in cold sulphuric acid has a deep red colour.

1-Chloro-2:4-dinitrobenzene and β-naphthylamine yield a *compound*, red prisms, m. p. 170—171°. Other compounds prepared in the course of this work are: a trinitro-derivative of phenyl-β-naphthylamine, melting and decomposing at 210°, and a dinitro-derivative, brown prisms, melting and decomposing at 170—180°.

F. C.

Improvements in the Manufacture of Nitrophenols.

DAVID BAIRD MACDONALD and JACKSON CALVERT (Brit. Pat., 126062 and 126084).—The formation of 2:4-dinitrophenol in the nitration of benzene with nitric acid in presence of mercuric nitrate is greatly facilitated by passing carbon dioxide either into the reaction mixture or through the benzene or nitric acid contained in a separate vessel, the mixed vapours then being led into the mixture of nitric acid and mercuric nitrate in the former case, or of benzene and mercuric nitrate, together with a small portion of the nitric acid, in the latter. The reaction is allowed to proceed for about six hours at 40—50°, and commercially pure dinitrophenol may be isolated from the reaction mixture by simply volatilising the more volatile constituents.

According to the second patent, air or oxygen, or a mixture of air and oxygen with or without carbon dioxide, may be substituted for the carbon dioxide there employed with similar results. [See, further, *J. Soc. Chem. Ind.*, 1919, 406A.] G. F. M.

Pinabietic Acid, a Resin Acid from the Sulphate Cellulose Liquors. OSSIAN ASCHAN and K. E. EKHOLM (*Finska Kem. Medd.*, 1918, pp. 8; from *Chem. Zentr.*, 1919, i, 285—286). —*Pinabietic acid*, $C_{20}H_{30}O_2$, shining needles, m. p. 176—178°, has been isolated from the resin acids of the "black liquor" of the sulphate cellulose factories. When dissolved in a mixture of chloroform and acetic anhydride, the acid yields, on addition of a little concentrated sulphuric acid, a purplish-red coloration which passes through violet and blue into black. With hydrochloric acid and ferric chloride, the coloration is violet-blue. The residue obtained after evaporation with nitric acid becomes orange-yellow on addition of ammonia, instead of violet as with abietic acid. The specific rotation depends greatly on the solvent, the acid being dextrorotatory when dissolved in aromatic hydrocarbons, but lævorotatory in solution in aliphatic hydrocarbons.   H. W.

Catalytic Racemisation of Ethyl *l*-Mandelate. ALEX. MCKENZIE and HENRY WREN (T., 1919, 115, 602—613).

The Bromination and Bromine Derivatives of Certain δ-Ketonic Esters. E. P. KOHLER and H. GILMAN (*J. Amer. Chem. Soc.*, 1919, 41, 683—692).—The course of the bromination of methyl γ-benzoyl-β-phenyl-αα-dimethylbutyrate,
$$CH_2Bz·CHPh·CMe_2·CO_2Me,$$
is found to depend on the temperature, the solvent, and the rate at which the bromine is added, the bromo-ester, saturated γ-lactones, and an unsaturated γ-lactone being formed.

γ-Benzoyl-β-phenyl-αα-dimethylbutyric acid is obtained by boiling together benzene, phenyl styryl ketone, and ethyl α-bromo*iso*butyrate with some zinc suspended in the liquid in a copper cage, and hydrolysing the product by methyl-alcoholic-aqueous sodium hydroxide. It has m. p. 159°, and forms an *oxime*, m. p. 184·5°. The methyl ester, m. p. 92°, b. p. 200°/25 mm., is formed in the usual way from the acid (compare A., 1911, i, 863). When the ester, dissolved in chloroform, is slowly treated with bromine in the cold, the chief product is methyl γ-bromo-γ-benzoyl-β-phenyl-αα-dimethylbutyrate, m. p. 125° (*ibid.*, 864). If the temperature is raised or the chloroform is removed by distillation instead of · evaporation in a current of dry air, methyl bromide is lost, and two stereoisomeric, saturated γ-lactones are formed (*ibid.*), whilst a crotonolactone is produced if the reaction is carried out in methyl alcohol or the bromine is added rapidly, thus:

$$CHBzBr·CHPh·CMe_2·CO_2Me \xrightarrow{-MeBr}$$

$$\begin{matrix} CHPh·CHBz \\ CMe_2\!\!-\!\!-CO \end{matrix}\!\!\!>\!O \xrightarrow{Br_2} \begin{matrix} CPh\!:\!CBz \\ CMe_2·CO \end{matrix}\!\!\!>\!O + 2HBr.$$
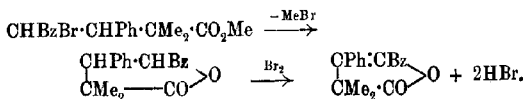
The original acid is easily converted into the δ-lactone (*ibid.*,

863), $CHPh\begin{array}{c}CH{=}CPh\\CMe_2{\cdot}CO\end{array}O$, by dissolving it in acetic anhydride containing a few drops of concentrated sulphuric acid. This lactone reacts with bromine in carbon tetrachloride to form an unstable dibromide which decomposes into the above bromo-ester and a saturated γ-lactone in methyl alcohol, but if bromination is carried out in methyl alcohol, an isomeric *bromo-ester*, m. p. 172°, is formed. The two esters both yield the γ-lactone, m. p. 115°, when left with methyl-alcoholic hydrogen bromide, but they behave differently on heating. The one with m. p. 125° decomposes at about 130° into the unbrominated ester, m. p. 92°, the corresponding acid, the γ-lactone, m. p. 115°, and the crotonolactone. The isomeride, m. p. 172°, decomposes at about 180° into benzoyl bromide, a small amount of the crotonolactone, and much uncrystallisable oil.

The above γ-*benzoyl-β-phenyl-aα-dimethylcrotonolactone* is obtained in pale yellow needles, m. p. 117°, by heating the original acid with bromine in carbon tetrachloride solution. The reaction proceeds briskly at first, but the final stage requires several hours, and it obviously follows a similar course to the bromination of the ester (above). The lactone may be reduced to the original acid by means of zinc and acetic acid. It gives a deep yellow solution in alcoholic potassium hydroxide, which deposits a yellow solid on acidifying, and this soon fades and produces the lactone again. With alcoholic hydrogen chloride, the lactone forms *ethyl* γ-*keto-γ-benzoyl-β-phenyl-aα-dimethylbutyrate*,

$$COPh{\cdot}CO{\cdot}CHPh{\cdot}CMe_2{\cdot}CO_2Et,$$
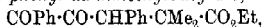
which crystallises in yellow needles, m. p. 93°, and may be hydrolysed to the free *acid*, m. p. 145°. The *dioxime* of this, m. p. 186°, is formed when the lactone is boiled with hydroxylamine hydrochloride and barium carbonate in alcohol.　　J. C. W.

Statics and Dynamics of the two Phthalyl Chlorides.

WILHELM CSÁNYI (*Monatsh.*, 1919, **40**, 81—92).—Phthalyl chloride exists in two tautomeric modifications, a solid and a liquid. The equilibrium in the melt is toward the side of the lower melting modification, and can only be reached from this side. The solid modification is the stable one. The equilibrium is independent of the temperature, hence the heat change accompanying the change from one modification to the other must be very small or zero. The equilibrium is set up extremely slowly at low temperatures, but with increase in temperature the velocity of the change to the stable form increases rapidly, so that at the boiling point it is almost instantaneous. The mean temperature-coefficient of the transition velocity is 1·6 for 10°. The velocity of the change was determined at 130°, the amount changed at measured intervals being deduced from the melting point of the mixture. It is shown that the reaction is unimolecular, and the velocity constant has the value 0·036. The natural melting point of the system is

practically identical with the melting point of the lower melting modification. An eutectic is formed at 8°, and consists of 23 parts of the higher melting variety to 77 parts of the lower melting variety.   J. F. S.

Constitution of Aliphatic γ-Ketonic Acids and the Aromatic o-Aldehydo- and o-Ketonic-carboxylic Acids and their Derivatives. KARL VON AUWERS and ANNA HEINZE (*Ber.*, 1919, **52**, [*B*], 584—601).—Some new examples of the application of optical measurements to the determination of chemical constitution.

Lævulic acid, b. p. 153°/14 mm., gives the following values: $E\Sigma_a - 0.03$, $E\Sigma_D - 0.01$, $E\Sigma_{\beta-a} + 2\%$, $E\Sigma_{\gamma-a} + 1\%$, calculated for the usual formula $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$. Its acetyl derivative, m. p. 78°, gives values which agree with the isomeric γ-lactone structure, $E\Sigma_a + 0.15$, $E\Sigma_D + 0.16$, $E\Sigma_{\beta-a} + 4\%$, $E\Sigma_{\gamma-a} \pm 0\%$, that is, it is really

γ-acetoxyvalerolactone, $OAc \cdot CMe \underset{O---CO}{\overset{CH_2 \cdot CH_2}{<}}$.
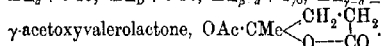
The phthalides show considerable exaltations, thus: phthalide itself, m. p. 73°, $E\Sigma_a + 0.64$, $E\Sigma_D + 0.67$, $E\Sigma_{\beta-a} + 27\%$; α-chloro-phthalide, from o-phthalaldehydic acid and thionyl chloride, m. p. 61°, $E\Sigma_a + 0.57$, $E\Sigma_D + 0.58$; diethylphthalide, m. p. 54°, b. p. 158°/17 mm. (Bauer, A., 1904, i, 417), $E\Sigma_a + 0.51$, $E\Sigma_D + 0.56$, $E\Sigma_{\beta-a} + 25\%$. The optical properties of the ψ-esters of o-aldehydo- or o-keto-acids agree with those of the phthalides, whilst the normal esters compare with the parent aldehyde or ketones. The ψ-esters are, therefore, phthalides, as Egerer and Meyer assumed (A., 1913, i, 269). Methyl o-aldehydo-benzoate, m. p. 97°, has $E\Sigma_a + 0.75$, $E\Sigma_D + 0.77$, $E\Sigma_{\beta-a} + 37\%$, $E\Sigma_{\gamma-a} + 41\%$ (benzaldehyde: $+0.99$, $+1.02$, $+45\%$, $+49\%$), and the

ψ-ester, α-methoxyphthalide, $CO \underset{O}{\overset{C_6H_4}{<}} > CH \cdot OMe$, m. p. 46—47°,

b. p. 145·5—146°/12 mm., compares with the above phthalides; $E\Sigma_a + 0.48$, $E\Sigma_D + 0.48$, $E\Sigma_{\beta-a} + 22\%$, $E\Sigma_{\gamma-a} + 22\%$. o-Propionyl-benzoic acid, m. p. 93°, gives values which suggest that in the molten state the acid contains some of the isomeric hydroxyethylphthalide; $E\Sigma_a + 0.52$, $E\Sigma_D + 0.53$, $E\Sigma_{\beta-a} + 22\%$. The *methyl* ester, $CO Et \cdot C_6 H_4 \cdot CO_2 Me$, from the silver salt and methyl iodide, b. p. 157—158°/19 mm., gives the values $E\Sigma_a + 0.53$, $E\Sigma_D + 0.55$, $E\Sigma_{\beta-a} + 26\%$, $E\Sigma_{\gamma-a} + 29\%$, which compare with those of propiophenone, $+0.43$, $+0.48$, $+29\%$, $+31\%$, whereas the ψ-ester, prepared by the action of the alcohol and sulphuric acid, is really a-methoxy-a-ethylphthalide, b. p. 157°/17 mm., $E\Sigma_a + 0.53$, $E\Sigma_D + 0.56$, $E\Sigma_{\beta-a} + 25\%$, $E\Sigma_{\gamma-a} + 26\%$. Methyl o-benzoyl-benzoate, m. p. 52°, $E\Sigma_a + 0.90$, $E\Sigma_D + 0.95$, $E\Sigma_{\beta-a} + 40\%$, $E\Sigma_{\gamma-a} + 45\%$, and the ethyl ester, m. p. 58°, $E\Sigma_a + 1.00$, $E\Sigma_D + 1.06$, $E\Sigma_{\beta-a} + 39\%$, compare with benzophenone, $E\Sigma_a + 0.98$, $E\Sigma_D + 1.09$, $E\Sigma_{\beta-a} + 44\%$, whilst the ψ-ester, m. p. 56°, $E\Sigma_a + 0.52$, $E\Sigma_D + 0.57$, $E\Sigma_{\beta-a} + 23\%$, $E\Sigma_{\gamma-a} + 23\%$, is really α-ethoxy-a-phenylphthalide.
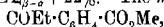
Ethyl hydrogen fumarate, m. p. 70°, $E\Sigma_a + 1.04$, $E\Sigma_D + 1.03$, $E\Sigma_{\beta-a} + 34\%$, shows greater exaltations than the normal ester, $E\Sigma_a + 0.64$, $E\Sigma_D + 0.67$, $E\Sigma_{\beta-a} + 25\%$, whereas the reverse is the case

with the phthalates ; ethyl hydrogen phthalate, $E\Sigma_a + 0\cdot42$, $E\Sigma_D + 0\cdot41$, $E\Sigma_{\beta-a} + 22\%$, ethyl phthalate, $E\Sigma_a + 0\cdot56$, $E\Sigma_D + 0\cdot58$, $E\Sigma_{\beta-a} + 22\%$. Methyl phthalate, whether prepared from the silver salt and methyl iodide, from the chloride and sodium methoxide or from the anhydride, alcohol, and hydrogen chloride, has the values $E\Sigma_a + 0\cdot56$, $E\Sigma_D + 0\cdot57$, $E\Sigma_{\beta-a} + 24\%$, $E\Sigma_{\gamma-a} + 27\%$.

Comparing ψ-esters with the normal esters, it appears that their boiling points are very close together, but that ψ-esters have the higher densities and lower refractive indices. For the details of densities and refractive indices, the original should be consulted.

J. C. W.

The Constitution of the Truxillic Acids and of Truxone.

HANS STOBBE (*Ber.*, 1919, **52**, [*B*], 1021—1028).—The formulæ

$$\begin{array}{cc} \text{Ph·CH·CH·CO}_2\text{H} & \text{CHPh·CH·CO}_2\text{H} \\ \text{CO}_2\text{H·CH·CHPh} & \text{CHPh·CH·CO}_2\text{H} \end{array}$$

and have been assigned to α- and β-truxillic acids. Whilst, however, the latter may be regarded as well established, the former is not so definitely proved, and depends chiefly on the determination of the molecular weight of the amyl ester, the failure to obtain benzil by oxidation, the formation of an abnormal polymeric anhydride which does not give a fluorescein, and the conversion into truxone. The molecular weight of the latter has not been directly determined, and its formulation is deduced from its relationship to truxene, truxene-quinone, and dihydrotruxone. Truxenequinone has, however, been shown to be identical with tribenzoylenebenzene, $C_{27}H_{12}O_3$, and since it is readily formed by the oxidation of truxene, it seems very probable that the latter is tribenzylenebenzene, $C_{27}H_{18}$, and that truxone has therefore the molecular formula $C_{27}H_{18}O_3$. Its formation from a number of substances, however, shows that the molecule of α-truxillic acid cannot contain more than eighteen carbon atoms, and this is supported by evidence from the molecular weights of ethyl dibromo-α-truxillate and ethyl hexachloro-α-truxillate.

To obtain further insight into the depolymerisation of the truxillic acids, the author has reinvestigated their action towards sulphuric acid; it is found that only the α-acid undergoes depoly-merisation with formation of truxone, and that the latter is not directly produced from α-truxillic acid, but is formed by the action of the sulphuric acid on the *trans*- or *cis*-cinnamic acid, which is the primary product of the change. The only positive evidence in favour of the usual formula for α-truxillic acid is thereby greatly discounted, and it appears possible to the author that the α- and β-acids are structurally identical, and therefore stereoisomerides, the difference in their behaviour being due to the relative positions of the phenyl and carboxyl groups with respect to the plane of the 4-carbon ring. Support for this hypothesis is deduced from a study of the absorption curves of α- and β-truxillic acids, which are found to be even more closely similar than those of the stereo-isomeric cinnamic acids. .   H. W.

The Addition of Nitromethane to Unsaturated Esters.
E. P. KOHLER and H. ENGELBRECHT (*J. Amer. Chem. Soc.*, 1919, **41**, 764—770).—The experiments on the interaction of alcoholic sodionitromethane and unsaturated ketones (A., 1916, i, 404) have now been extended to $\alpha\beta$-unsaturated esters. Deep orange or red solutions are obtained which, on acidification, yield red oils which do not crystallise and cannot be purified by distillation in a vacuum. Similar results are obtained when the condensation takes place in presence of small amounts of feebly basic reagents, such as sodamide, piperidine, potassium acetate, etc. These red oils are insoluble in sodium carbonate, and their colour is not affected on acidification. They may be heterocyclic compounds formed by elimination of sodium methoxide from the metallic derivatives. Thus, in the case of dimethyl benzylidenemalonate,

$$\begin{array}{ccc} \text{CHPh}\text{------------}\text{CH·CO}_2\text{Me} & \text{. CHPh------CH·CO}_2\text{Me} \\ \underset{\text{CH:NO·ONa   Me}_.\text{O·CO}}{\underbrace{\qquad\qquad\qquad}} & \rightarrow \quad \underset{\text{CH:NO·O·CO}}{\underbrace{\qquad\qquad}} \quad +\text{NaOMe,} \end{array}$$
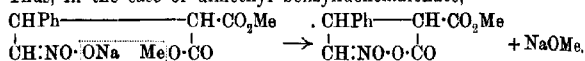
It was finally shown that, in order to isolate the additive product of nitromethane and to avoid the formation of these red oils, the experiments should be made in dry methyl-alcoholic solution in presence of sodium methoxide, the mixture immediately neutralised with a little glacial acetic acid, and saturated with hydrogen chloride. Under these conditions, dimethyl benzylidenemalonate gives methyl γ-nitro-β-phenylethylmalonate,

$$\text{NO}_2\text{·CH}_2\text{·CHPh·CH(CO}_2\text{Me)}_2,$$

stout prisms, m. p. 63°, which is identical with the additive product of methyl sodiomalonate and β-nitrostyrene; this is an example of a new type of reaction, which is being further investigated. With alkalis, this substance is decomposed, whilst boiling hydrochloric acid yields phenylsuccinic acid. Bromine in carbon tetrachloride gives a monobromo-derivative, m. p. 158°.

The additive product of nitromethane and dimethyl cinnamylidenemalonate, $\text{CHPh:CH·CH(CH}_2\text{·NO}_2)\text{·CH(CO}_2\text{Me)}_2$, can also be obtained in benzene solution with a yield of 65%. In methyl alcohol, the yield is 87%. The nitro-ester crystallises in square plates, m. p. 74—75°.

The authors have prepared esters of benzoylacrylic acid by brominating esters of benzoylpropionic acid, and subsequently eliminating hydrogen bromide. *Methyl benzoylacrylate* was obtained in 92% yield as a yellow oil, b. p. 191° at 40 mm., and solidifying at 32°.

Methyl β-nitro-α-phenacylpropionate,

$$\text{COPh·CH}_2\text{·CH(CH}_2\text{·NO}_2)\text{·CO}_2\text{Me,}$$

melts at 57°.

Two formulæ are possible for a substance of this type, because the ethylenic linking in the ester of benzoylacrylic acid is conjugated both with the carbonyl and with the carboxyl group. The foregoing constitution assigned to it is supported by the fact that when sodiomalonic esters combine with methyl benzoylacrylate, the sodium atom becomes attached to the carbon atom furthest from the carboxyalkyl group.

With boiling hydrochloric acid it yields benzoylpropionic acid. Bromine in chloroform gives rise to two isomeric monobromo-derivatives, separable owing to their differing solubility in cold methyl alcohol. The sparingly soluble one crystallises in plates, m. p. 125°. The other forms needles, m. p. 59°.　　　　　　F. C.

Bile Acids. V. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1919, **104**, 284—292. C6mpare A., 1914, i, 487).—The *iso*dioxime of bilianic acid when heated with 20% hydrochloric acid yields a substance, isolated by means of its copper salt, which crystallises in white needles decomposing at 228—230°. It is believed that this product is *aminocarboxybilianic acid isooxime*, $C_{24}H_{38}O_9N_2$, formed by the opening of only one of the two lactam rings present in bilianic acid. Such an acid should contain four carboxyl groups, three of which were present in bilianic acid, but only three were titratable by direct means. It is considered that the fourth is protected by the adjacent amino-group, since an increased titration value was obtained after treatment with formaldehyde by the technique of Sörensen. Cholic acid oxime, $C_{24}H_{37}O_7N$, begins to decompose at 160°. The oxime treated with strong sulphuric acid on the water-bath gave the *iso*oxime, $C_{24}H_{37}O_7N$, long, hexagonal needles, decomp. 273—275°. By the action of hydrochloric acid on the *iso*oxime, a substance, $C_{24}H_{39}O_8N$, was obtained in rhombohedra, m. p. 194—195°. This is apparently *aminocarboxycholic acid*. After melting, it sets again, and finally decomposes at 274—275°, the decomposition point of the *iso*oxime. These experiments support the work of Borsche and Rosenkranz (this vol., i, 276) on the structural relationship between bilianic acid and cholic acid.　　　　　　J. C. D.

Attempted Synthesis of Fisetol. ADOLF SONN (*Ber.*, 1919, **52**, [B], 923—928).—The synthesis of fisetol (ω-hydroxyresacetophenone) has been attempted by several methods, which, however, have not been completely successful (compare Tambor and Du Bois, A., 1918, i, 395).

Chloroacetonitrile and resorcinol monomethyl ether react in ethereal solution under the influence of zinc chloride and dry hydrogen chloride to yield the 2-*methyl* and 4-methyl ether of ω-chlororesacetophenone, which are separated by taking advantage of the volatility of the latter with steam; the former has m. p. 173—174° (uncorr.). Similarly, bromoacetonitrile and resorcinol dimethyl ether yield ω-*bromoacetoresorcinol dimethyl ether*, m. p. 102—104° after previous softening, which is probably converted by potassium acetate into the corresponding *acetate*, prisms, m. p. 75°. Resorcinol and bromoacetonitrile yield a *product*, m. p. 127° after softening, but, as in the case of the dimethyl ether, the analytical results point to a partial displacement of bromine during the condensation. ω-*Phenoxyresacetophenone*,

$$C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot OPh,$$
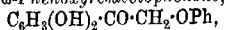
forms coarse, shining plates, has m. p. 204—205° after softening at

200° (attempts to remove the phenyl group were unsuccessful); its *dimethyl ether* forms thin prisms or needles, m. p. 115° after previous softening. ω-*Ethoxyresacetophenone* has m. p. 136—137° after softening; its *diethyl ether*, coarse prisms, and *dimethyl ether*, irregular plates, have m. p.'s 66° and 56—57° respectively.

<div align="right">H. W.</div>

The Preparation of β-Aminopropiophenone. WILLIAM J. HALE and EDGAR C. BRITTON (*J. Amer. Chem. Soc.*, 1919, **41**, 841—847).

—Amino-derivatives of ketones cannot be satisfactorily prepared by the action of ammonia on the corresponding halogen derivatives owing to the further substitution of the hydrogen of the ammonia. Amides of ketonic acids behave abnormally in the Hofmann reaction, and give rise to internal condensation products (compare Biedermann, A., 1892, 471).

Gabriel prepared β-aminopropiophenone from *p*-bromopropyl-phthalimide. This was converted into the corresponding alcohol, acid, and acid chloride, which by the Friedel and Craft reaction and subsequent hydrolysis yielded the desired product (A., 1908, i, 181).

The author has prepared β-phthaliminopropionic acid from the *iso*amyl ester of β-chloro- or iodo-propionic acid. The yield, however, was only 40%. In order to avoid the formation of substituted phthalamic acids, the hydrolysis is effected with 40% hydrobromic acid instead of sodium hydroxide. The method finally adopted is indicated by the scheme β-iodopropionic acid ⟶ β-iodopropionyl chloride ⟶ β-iodopropiophenone ⟶ β-phthaliminopropiophenone ⟶ β-aminopropiophenone. The yields in the last stages are 90%, 68%, and 95%.

The β-chloro-derivative of propionic acid may also be used, but its preparation is less easy than that of the iodo-derivative. *iso*A*myl* β-*chloropropionate* is miscible with most organic solvents except light petroleum, and boils at 207—208°/740 mm. The corresponding *iodo*-compound has b. p. 183°/140 mm. (slight decomp.). *iso*A*myl* β-*phthaliminopropionate*, m. p. 61°, was obtained in a 70% yield from either of the two foregoing compounds.

β-Chloropropiophenone decomposes on distillation in a vacuum into hydrogen chloride and phenyl vinyl ketone.

β-*Iodopropiophenone*, m. p. 61°, is insoluble in water and crystallises from alcohol. The acid chloride of β-iodopropionic acid. is exceedingly irritating to the eyes, and readily decomposes on distillation.

<div align="right">F. C.</div>

A New Synthesis of Styryl Methyl Ketone. G. LANGLOIS (*Compt. rend.*, 1919, **168**, 1052—1054).

—Acetyl chloride reacts with styrene in the presence of stannic chloride to give β-chloro-β-phenylethyl methyl ketone, which, on the addition of diethyl aniline, loses the elements of hydrogen chloride, giving styryl methyl ketone.

<div align="right">W. G.</div>

Constitution of Hydroxy- and Hydroxylamino-anthra-quinone Salts. R. SCHOLL (*Ber.*, 1919, **52**, [B], 565—567).

—In part, a denial of Baudisch's claim to priority (this vol., i, 211).

When a solution of 1-hydroxylaminoanthraquinone in alcohol is mixed with about two equivalents of sodium ethoxide and left in an atmosphere of nitrogen, a green *mono-sodium* salt is deposited. This shows that the compound behaves as a benzenoid structure (I) rather than in the isomeric form (II), which would give a disodium salt.

(I.)   (II.)
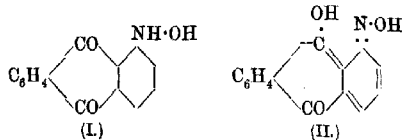
J. C. W.

Cyclic Compounds from Anthraquinone-1-sulphonic Acid.

FRITZ ULLMANN and PAUL KERTÉSZ (*Ber.*, 1919, **52**, [*B*], 545—558).—Anthraquinone is sulphonated in the presence of mercury, and the potassium anthraquinone-1-sulphonate (Iljinsky, A., 1904, i, 176; Schmidt, *ibid.*, 256) is heated with a mixture of phosphorus pentachloride and oxychloride at 120°. *Anthraquinone-1-sulphonyl chloride* (compare MacHoul, *Diss.*, Freiburg, 1880) crystallises from nitrobenzene or toluene in golden-yellow prisms, m. p. 218° (corr.), changes into 1-chloroanthraquinone when kept at 220°, and is hydrolysed by boiling water to anthraquinone-1-*sulphonic acid*. This forms colourless leaflets, m. p. 214° (corr.), and yields a *barium* salt, insoluble, white needles, a *calcium* salt, soluble in boiling water, a golden-yellow *lead* salt, crystallising from boiling water, a *hydrazine* salt, $N_2H_4(C_{14}H_8O_5S)_2$, and an *aniline* salt, pale yellow needles, m. p. 291°. (The *aniline* salt of anthraquinone-2-sulphonic acid is silvery-white and has m. p. 314°.)
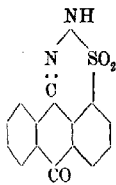
The reactions of the sulphonyl chloride with various bases are described. Hydrazine hydrate reacts at 30° to give the *anhydride* of anthraquinone-1-*sulphonhydrazide* (annexed formula), which crystallises from aniline or nitrobenzene as a yellow powder, and yields a *sodium* salt, yellow leaflets, a *silver* salt, pale yellow leaflets, a *methyl* derivative (with methyl sulphate), silvery leaflets, decomp. 239°, and an *acetyl* derivative, pale yellow needles, m. p. 237° (decomp.). Ammonia gives the *anhydride* of 1-anthraquinonesulphonamide (annexed formula), which crystallises from pyridine or nitrobenzene in pale yellow, felted needles, m. p. 321° (corr.). Aniline gives *anthraquinone-1-sulphonanilide*, golden-yellow needles from toluene, m. p. 216° (corr.), and methylaniline yields *anthraquinone-1-sulphon-methylanilide*, $C_6H_4{<}{CO \atop CO}{>}C_6H_3 \cdot SO_2 \cdot NMePh$, pale yellow leaflets, m. p. 205°.
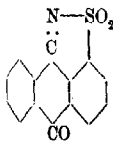
On nitration, the potassium salt of anthraquinone-1-sulphonic acid gives a mixture of 5- and 8-nitroanthraquinone-1-sulphonic acids. The former separates directly from the hot nitrating mixture, whilst the latter crystallises slowly when the filtrate is kept (compare Schmidt, *loc. cit.*). 5-Nitroanthraquinone-1-sulphonic acid forms a golden-yellow *potassium* salt, a white *barium* salt, and a *sulphonyl chloride*, yellow needles, m. p. 277° (corr.), which reacts with ammonia to give the *anhydride* of 5-*nitroanthraquinone*-1-*sulphonamide*, this crystallising from nitrobenzene in pale brown needles, m. p. 425°, and yielding the corresponding 5-*amino*-compound, dark violet leaflets, on reduction with alkaline hypo-sulphite. 8-Nitroanthraquinone-1-sulphonic acid forms a *potassium* salt, twice as soluble as the isomeride, and a *sulphonyl chloride*, yellow needles, m. p. 245°, which yields the *anhydride* of 8-*nitro-anthraquinone*-1-*sulphonamide*, m. p. 314° (corr.). The nitro-compounds may be reduced by means of potassium sulphide; *potassium* 5- and 8-*aminoanthraquinone*-1-*sulphonates* crystallise in violet needles, the 8-isomeride being the more soluble. The constitution and purity of the nitrated acids were elucidated by boiling them with hydrochloric acid and sodium chlorate, whereby they yielded 1-*chloro*-5-*nitroanthraquinone*, yellow, felted needles, m. p. 314° (corr.) (convertible into the known 1-nitro-5-amino-anthraquinone), and 1-*chloro*-8-*nitroanthraquinone*, m. p. 263° (corr.).   J. C. W.

Reduction Products of Hydroxymethylenecamphor. II. Mechanism of the Hydrogenation of Hydroxymethylene-camphor with Hydrogen and Nickel. HANS RUPE and ARTHUR AKERMANN (*Helv. Chim. Acta*, 1919, **2**, 205—221. Compare this vol., i, 29).—The hydrogenation of hydroxymethylenecamphor in the presence of a specially prepared nickel catalyst can be made use of in a study of the kinetics of such reactions, and a series of experiments with this aim are now described. A graphic representation of the hydrogen absorbed from time to time shows that the curves are nearly hyperbolic when the abscissæ, x, are taken from the values, time × weight of catalyst/initial weight of hydr-oxymethylenecamphor, and the ordinates, y, are the percentages of hydrogen absorbed, calculated on the theoretical requirement. These curves are treated mathematically, and, after making corrections for probable disturbing factors, such as secondary reactions caused by nickel compounds, it appears that the main reaction is a bimolecular one. That is, not only does the quantity of hydr-oxymethylenecamphor fall off, but the amount of hydrogen trans-ferred as well, or, in other words, the catalyst continually decreases in activity. This explains why such a large quantity of nickel is required in this case to achieve a rapid and complete reduction.

In this reduction, as in so many similar cases, much more hydrogen is absorbed than is theoretically required, but, as a matter of fact, the reduction is actually complete when only about 80—90% of the required volume of gas has disappeared. This is

not due to experimental errors, but chiefly to the activation of the water by the nickel. J. C. W.

Reduction Products of Hydroxymethylenecamphor. III. New Reactions of Methylenecamphor. HANS RUPE and ARTHUR AKERMANN (*Helv. Chim. Acta*, 1919, **2**, 221—233). Com-

pare this vol., i, 29).—When camphylcarbinol is warmed with sodium in benzene solution, a new derivative, s-*dicamphylethane*,
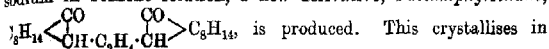
$$C_8H_{14}{<}^{CO}_{CH \cdot C_2H_4 \cdot CH}{>}^{CO}_{}C_8H_{14},$$ is produced. This crystallises in

slender, white prisms, m. p. 209—211°, and its constitution is revealed by the fact that it may be obtained from camphylmethyl bromide by the Fittig and Wurtz method. It is assumed that water is eliminated from the carbinol, giving methylenecamphor and hydrogen (from the sodium), and that either two molecules of this compound condense and then combine with hydrogen, or one molecule is reduced to methylcamphor, which condenses with the methylenecamphor. The compound can also be obtained by boiling solutions of methylenecamphor in benzene or toluene with sodium, and then treating the product with water. In this case, the necessary hydrogen is supposed to be derived from an enolic form of the compound obtained by the union of two molecules of methylenecamphor. The fact that both series of reactions proceed better in moist benzene supports the given interpretations of the mechanism.

In the Fittig-Wurtz reactions, and in the above processes when moisture is excluded, small quantities of an *isomeride* are formed, which is slightly less soluble in light petroleum and crystallises in glistening, crossed prisms, m. p. 258—259°. Probably it has the

formula, $C_8H_{14}{<}^{CO}_{CMe \cdot CH_2 \cdot CH}{>}^{CO}_{}C_8H_{14}.$
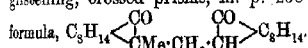
Chloromethylenecamphor (A., 1916, i, 409) also reacts readily with sodium in ethereal solution, giving the *cis-* and *trans*-modifications of *dicamphoethandiene*,

$$C_8H_{14}{<}^{CO}_{C}\quad\quad\quad C_8H_{14}{<}^{CO}_{C}$$
$$C_8H_{14}{<}^{C:CH \cdot CH}_{CO}\quad and \quad {}^{CH \cdot CH:C}_{CO}{>}C_8H_{14}.$$
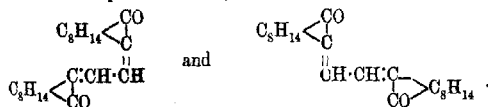
The *cis*-modification crystallises from light petroleum in orange-yellow tetrahedra, m. p. 238—239·5°, whereas the *trans*-isomeride is insoluble and separates best from glacial acetic acid in slender, greenish-yellow needles, m. p. 282—283°.

Camphylmethyl bromide does not react at all readily with magnesium, and its reaction with magnesium phenyl bromide is also not so vigorous as in the case of chloromethylenecamphor. The product, benzylcamphor, was also obtained with about the same optical properties by the reduction of benzylidenecamphor with sodium amalgam. J. C. W.

Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. I. Position Isomerism and Optical Activity of Naphthyliminocamphors and Derivatives of Phenyliminocamphor. BAWA KARTAR SINGH and JATINDRA KUMAR MAZUMDAR (T., 1919, 115, 566—576).

Genetic Relationships of the Terpenes. OSSIAN ASCHAN (*Finska Kem. Jubiläumsnummer*, 1918, pp. 15; from *Chem. Zentr.*, 1919, i, 285).—A concise résumé of the chemistry of the terpenes. H. W.

New Terpene in Finnish Turpentine. OSSIAN ASCHAN (*Technikern*, 1918, pp. 3; from *Chem. Zentr.*, 1919, i, 284).—A new terpene hydrocarbon has been obtained by the fractional distillation of Finnish turpentine with steam; it has b. p. 163—165°, D_4^{20} 0·8628, $[\alpha]_D$ +7·70°, and is a bicyclic, simply saturated terpene closely related to pinene. It yields pinene nitrosochloride with amyl nitrite and hydrochloric acid. H. W.

Action of Finely Divided Metals on Pinene Vapour. PAUL SABATIER, ALPH. MAILHE, and G. GAUDION (*Compt. rend.*, 1919, 168, 926—930).—The metals used were copper, nickel, cobalt, and iron. When pinene vapour is passed over any of these metals at 350°, there is no evolution of gas, but a liquid is obtained which is less volatile than the original pinene and consists of terpenes isomeric with pinene and a small amount of polyterpenes. At higher temperatures there is an evolution of gas, the amount of which varies with the temperature and the nature of the metallic catalyst. With copper at 500° there is an abundant evolution of a gas, which is a mixture of hydrogen and olefines. With copper at 600—630° there is a still more marked evolution of gas, whilst the liquid product consists of a mixture of isoprene, olefines and diolefines, terpenes, and aromatic hydrocarbons, such as toluene, *m*-xylene, cymene, cumene, and methylethylbenzene. The yield of aromatic hydrocarbons was in one case 31% of the pinene used. With reduced nickel at 600°, a very energetic decomposition of the pinene occurs, a gas being evolved rich in hydrogen, carbon is deposited, and very little liquid product is obtained. With cobalt at 600°, the results obtained are intermediate between those obtained with nickel and copper, whilst reduced iron is similar to nickel in its effect. W. G.

Finnish Turpentine. V. Formation of Terpin Hydrate and Terpineol. OSSIAN ASCHAN (*Bidrag känn. Finlands natur och folk*, 1918, 77, pp. 30; from *Chem. Zentr.*, 1919, i, 284).—The author has endeavoured to find new methods of preparing terpin from pinene and dipentene. Preliminary experiments on the action of sulphuric acid of varying concentration on oil of turpentine without cooling showed that terpin (which is probably transiently formed under all conditions when pinene is converted

into dipentene by acids) was certainly produced at the ordinary temperature, but that at the high concentration, and possibly increased temperature, water was almost immediately eliminated and dipentene formed. It is important that stirring and cooling should be very efficient, thereby preventing decomposition of the terpin hydrate formed by the acid. With efficient stirring (ten hours) and using 45% sulphuric acid, 53·2% of the theoretical yield of terpin was obtained; during the greater part of the time, the temperature must be maintained at +1°. *trans*-Terpin is formed as a by-product. Terpin is also produced by the action of sulphuric acid (45%) on nopinene (from American oil of turpentine).

Terpin may also be obtained by addition of water to dipentene (1 part) by treatment with sulphuric acid (55%; 6 parts) at −6°; the crude product is remarkably pure, but may contain *trans*-terpin. The conversion of terpin hydrate by loss of water into terpineol is best effected by the action of oxalic acid solution (0·5%). The transformation of terpineol into pinene by means of formic acid is so successful that the process appears capable of technical application. An almost quantitative yield of terpin hydrate is obtained from terpineol (1 part) by the action of sulphuric acid (10%; 5 parts), the mixture being kept well stirred and cooled by ice. Terpin hydrate can be prepared in good yield from the fraction of Finnish turpentine, b. p. 155—167°, which contains the terpenes related to pinene. H. W.

Finnish Turpentine. VI. The Components of High Boiling Point.

Ossian Aschan (*Bidrag känn. Finlands natur och folk*, 1918, 77, pp. 88; from *Chem. Zentr.*, 1919, i, 284—285).— A specimen of turpentine and a resin distillate obtained in the manipulation of the resin of *Pinus sylvestris* have been investigated, and terpene alcohol and cadinene have been obtained. The question whether cadinene exists as such in the fraction, b. p. 125—130°/9 mm., or whether its hydrochloride is formed by the action of hydrogen chloride on another sesquiterpene, remains undecided. H. W.

Constituents of Higher Boiling Point in Finnish Turpentine.

Ossian Aschan (*Finska Kem. Medd.*, 1918, pp. 3; from *Chem. Zentr.*, 1919, i, 285).—Fractions b. p. 210—220° and ca. 260° have been observed in Finnish turpentine in the products of the tar ovens and in those obtained by the distillation of resin with steam; they appear to consist of terpene alcohol and a sesquiterpene, and resemble that obtained from pine resin (preceding abstract). An unsaturated terpene alcohol, $C_{10}H_{17}·OH$, has been isolated which is not identical with terpineol, but is possibly a mixture of the latter with other terpene alcohols. A sesquiterpene, $C_{15}H_{24}$, b. p. 260—263°/760 mm., D_4^{20} 0·9187, has also been obtained. It is unsaturated towards potassium permanganate, bromine, and hydrogen chloride, and is converted by the latter into cadinene dihydrochloride, m. p. 117—118°. Since cadinene, obtained from

this hydrochloride, has b. p. 271°, it cannot be identical with the original substance.   H. W.

The Sesquiterpene Fraction in the Volatile Portions of Pine Resin. OSSIAN ASCHAN (*Finska Kem. Medd.*, 1918, pp. 2; from *Chem. Zentr.*, 1919, i, 285).—A new terpene has been isolated from a distillate obtained during the manipulation of pine resin. Its *dihydrochloride*, $C_{15}H_{26}Cl_2$, forms shining, rhombic leaflets, m. p. 85—86°. It is possibly a bicyclic sesquiterpene, and may be related to cadinene.   H. W.

Some Constituents of French and American Rosins. EDMUND KNECHT and EVA HIBBERT (*J. Soc. Dyers*, 1919, 35, 148—154).—By repeated crystallisation from glacial acetic acid and alcohol, two pimaric acids, $C_{20}H_{30}O_2$, are isolated from French and American rosins, that from the former forming large, colourless crystals, m. p. 161°, a_D —80°, and that from the latter melting at the same temperature and having a_D +79°. The two acids differ in certain particulars, and are probably not optical isomerides. On heating in a vacuum or in a stream of carbon dioxide, both acids are converted into rosin-like anhydrides by the loss of a molecule of water from two of acid. The hydration of the anhydride of *l*-pimaric acid takes place slowly at the ordinary temperature by the action of water, and when it is crystallised from water-absorbing solvents, such as alcohol or acetic acid, inactive pimaric acid is obtained which, by ebullioscopic methods, gives figures indicating a double molecular weight. Resolution of the acid is effected by means of *d*-tetrahydroquinaldine. By the action of bromine in carbon tetrachloride solution, both *d*- and *l*-pimaric acids give crystalline tribromo-substitution products, m. p. 115—118°, whilst with nitrous acid, greenish-blue, crystalline nitrosites, m. p. 99°, are obtained. When exposed to the air, *l*-pimaric acid slowly absorbs oxygen to the extent of two atomic proportions, and on distillation with aluminium, a hydrocarbon, $C_{19}H_{30}$, is produced, probably identical with or analogous to abietene or colophene. The rosins themselves probably consist mainly of anhydrides, hydration being a preliminary to the crystallisation of the rosin acids.   G. F. M.

Synthetic Glucosides. III. A Contribution to the Constitution of Internally Complex Salts. P. KARRER, C. NÄGELI, and H. WEIDMANN (*Helv. Chim. Acta*, 1919, 2, 242—265. Compare A., 1916, i, 832; 1917, i, 539).—I. *Constitution of Internally Complex Salts* [with L. WILBUSCHEWICH].—It is now generally accepted that the metallic atom in internally complex salts of the α-amino- or α-hydroxy-acids is bound, not only to the carboxyl group, but to the α-substituent as well. That being so, it should be possible to obtain isomeric derivatives by the action of a suitable halogen compound on the salt, according to the scheme:

$$\begin{array}{c} R \cdot CH \cdot NH \\ \underset{CO\text{---}C}{\overset{r}{\diagdown}} M + R'X \longrightarrow \underset{CO_2H}{\overset{R \cdot CH \cdot NHR'}{}} + \underset{CO_2R'}{\overset{R \cdot CH \cdot NH_2}{}} , \end{array}$$
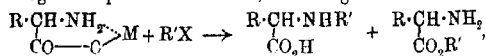
in which ·OH might be written instead of ·NH₂. An indication that such a reaction might take place has already been given, namely, in the formation of tetra-acetylglucose salicylate and the tetra-acetylglucoside of salicylic acid by the action of acetobromoglucose on silver salicylate, and it is now shown that silver anthranilate reacts with ethyl iodide in warm toluene to form a mixture of *N*-ethylanthranilic acid and ethyl anthranilate.

In order to obtain pairs of isomerides at all, search must be made for a suitable halogen derivative. For example, silver salicylate and ethyl iodide only give ethyl salicylate. It is somewhat remarkable that acetobromoglucose is more suitable than any other derivative tested so far. This is of interest, because it opposes another interpretation of the reaction, which, without reference to internally complex salts, would suggest that any change at the *α*-amino- or *α*-hydroxyl group might be preceded by attachment of the haloid as such. Acetobromoglucose has practically no tendency to form quaternary salts with amines.

It is generally assumed that the metal is attached to the carboxylic residue by a main valency and to the amino- or hydroxyl group by residual affinity. The preponderance of ester in most of the above reactions is in keeping with this view, but it is possible to represent the salts as desmotropes, thus:

$$\begin{array}{ccc} \text{R·CH--NH}_2 & \rightleftarrows & \text{R·CH·NHM} \\ | \quad \vdots & & | \\ \text{CO·OM} & & \text{CO·OH} \end{array}$$
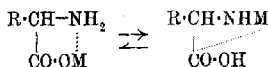
II. *Glucosides of α-Hydroxycarboxylic Acids.*—The silver salts of all the *α*-hydroxy-acids investigated so far react with acetobromoglucose to give isomerides, as in the case of salicylic acid. *Ammonium β-tetra-acetyl-d-glucosidoglycollate,*

$$CO_2(NH_4)·CH_2·O·C_6H_7O_5Ac_4,$$
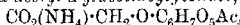
from silver glycollate, crystallises in concentric groups of felted needles, with about 2 mols. EtOH, which it loses at 95—100°, and has m. p. 157°, $[α]_D^{18}$ −35·6°. It yields β-*d*-glucosidoglycollic acid on hydrolysis with baryta or ammonia (Fischer and Helferich, A., 1911, i, 675).

Silver lactate gives *tetra-acetyl-*d-glucose dl-*lactate,* felted needles, m. p. 174°, $[α]_D^{16}$ −3·23°, and *ammonium β-tetra-acetyl-*d-*glucosido-*dl-*lactate,* m. p. 165°, $[α]_D^{16}$ −34·92°, which yields d-*glucosido-*dl-*lactic acid,* $[α]_D^{17}$ −36·58°, on hydrolysis.

The active and inactive mandelic acids give the following compounds: *β-tetra-acetyl-*d-*glucosido-*dl-*mandelic acid,* felted, white needles, m. p. 130—150°, $[α]_D^{15}$ from −36·97° to −43·46° with different preparations, the corresponding *derivative* of *d*-mandelic acid, $C_6H_7O_5Ac_4·O·CHPh·CO_2H$, highly refractive needles, m. p. 166°, $[α]_D^{14}$ −5°, and the *derivative* of *l*-mandelic acid, white needles, m. p. 132°, $[α]_D^{15}$ −82·4°; *β-tetra-acetyl-*d-*glucose* d-*mandelate,* OH·CHPh·CO₂·C₆H₇O₅Ac₄, snow-white needles, m. p. 163°, $[α]_D^{14}$ +5·13° (yield four times as great as that of the glucoside), and the l-*mandelate,* m. p. 134°, $[α]_D^{15}$ −63·09°, which is much more

soluble in alcohol than the isomeride, it being possible to separate the inactive dl-mandelate into the two esters by fractional crystallisation. The tetra-acetates may be hydrolysed by baryta or dilute ammonia solutions to the following: d-*glucosido*-dl-*mandelic acid*, $C_6H_{11}O_5\cdot O\cdot CHPh\cdot CO_2H$, also designated *prulaurasinic acid*, because of its relationship to the cyanogetic glucoside, prulaurasin, a white, hygroscopic powder, crystallising with 1EtOH, $[\alpha]_D^{11} - 28\cdot17 - 33\cdot18°$, which is hydrolysed by emulsin, but does not reduce Fehling's solution, and forms a very hygroscopic *ammonium* salt, $0\cdot5H_2O$, $[\alpha]_D^{11} - 36\cdot12°$; and d-*glucosido*-l-*mandelic acid*, $[\alpha]_D^{15} - 138\cdot6°$, and u-*glucosido*-d-*mandelic acid*, $[\alpha]_D^{17} + 51\cdot39°$, also called *prunasinic acid* and *sambunigrinic acid* respectively.

III. *Glucosides of Anthranilic Acid.*—Silver anthranilate reacts with acetobromoglucose to form *tetra-acetylglucose anthranilate*, $NH_2\cdot C_6H_4\cdot CO_2\cdot C_6H_7O_5Ac_4$, m. p. 177°, $[\alpha]_D^{11} - 58\cdot12°$, and N-*tetra-acetylglucosidoanthranilic acid*, $CO_2H\cdot C_6H_4\cdot NH\cdot C_6H_7O_5Ac_4$, white needles, m. p. 181°, $[\alpha]_D^{17} - 63\cdot89°$. The latter is a representative of the somewhat obscure group of N-glucosides. It may be hydrolysed by methyl-alcoholic ammonia to the very hygroscopic *ammonium* N-d-*glucosidoanthranilate*, $[\alpha]_D^{11} - 85\cdot66°$, which reduces Fehling's solution, and may be converted into the *silver* salt, but the free acid is too unstable to be isolated. In one hydrolysis, *ammonium* N-*acetyl*-d-*glucosidoanthranilate* was formed,

$$C_6H_{11}O_5Ac\cdot NH\cdot C_6H_4\cdot CO_2\cdot NH_4,$$
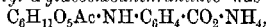
in stout, limpid crystals, m. p. 80—85°.　　　　　J. C. W.

The Tannin of the Canadian Hemlock (Tsuga Canadensis, Carr.). RODGER JAMES MANNING and MAXIMILIAN NIERENSTEIN (T., 1919, **115**, 662—673).

Cyclic Ethers from o-Allyl Phenols ; Methylenecoumarans [1-Methylene-1 : 2-dihydrobenzofurans]. ROGER ADAMS and R. E. RINDFUSZ (*J. Amer. Chem. Soc.*, 1919, **41**, 648—665).—The following series of reactions with o-allylphenol has been studied: (a) acetylation, (b) bromination, and (c) treatment of the dibromide with alcoholic potassium hydroxide. These are the reactions involved in the production of flavones by Kostanecki's method from o-acetoxyphenyl styryl ketones, and it was expected that in this case the parent of the flavones, namely, "chromene" (I), would be formed. Instead, the last operation takes a different course, and the product is 1-methylenecoumaran (II).

$$C_6H_4 \underset{O——CH}{\overset{CH_2\cdot CH}{<}} \qquad\qquad C_6H_4 \underset{O}{\overset{CH_2}{<}} {>} C{:}CH_2.$$

　　　(I.)　　　　　　　　　　　　　　(II.)
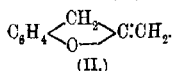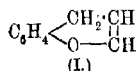
The formation of the methylenecoumaran appears to be a general reaction, and the mechanism of the process was proved as follows. When the o-acetoxy-βγ-dibromopropylbenzene is treated with one molecular proportion of sodium ethoxide, the acetyl group is eliminated and a monobromo-cyclic ether formed, which yields the known 1-methylcoumaran on reduction with zinc and hydrochloric

acid, and 1-methylenecoumaran when boiled with alcoholic potassium hydroxide. The reactions can only be interpreted as follows:

$$C_6H_4{\textstyle<}^{CH_2\cdot CHBr\cdot CH_2Br}_{OAc} \quad \rightarrow \quad C_6H_4{\textstyle<}^{CH_2\cdot CHBr\cdot CH_2Br}_{OK}$$

$$\qquad\qquad (a.) \qquad\qquad\qquad\qquad\qquad \downarrow$$

$$C_6H_4{\textstyle<}^{CH_2}_{O-\!\!-}{\textstyle>}C{:}CH_2 \quad \leftarrow \quad C_6H_4{\textstyle<}^{CH_2}_{O-\!\!-}{\textstyle>}CH\cdot CH_2Br$$

$$\qquad\qquad\qquad\qquad\qquad\qquad (b.)$$
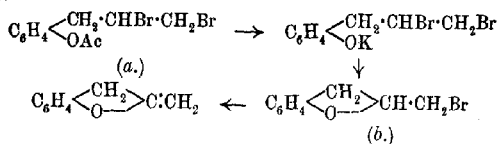
o-Acetoxyallylbenzene, from *o*-allylphenol and acetic anhydride, has b. p. 123—124°/20 mm., D^{24} 1·031, n_D^{20} 1·508, and its *dibromide* (a) forms white crystals, m. p. 42°; 1-*bromomethylcoumaran* (b) has b. p. 144—145°/20 mm., D^{25} 1·453, n_D^{20} 1·575; and 1-*methylene-coumaran* is a pleasant-smelling oil, b. p. 93—94°/20 mm., 196—197°/744 mm., D^{24} 1·050, n_D^{22} 1·555, which reacts with bromine in carbon disulphide at 0° to form 1-*bromomethylenecoumaran*,

$$C_6H_4{\textstyle<}^{CH_2}_{O-\!\!-}{\textstyle>}C{:}CHBr, \quad \text{b. p.} \quad 134—138°/25 \text{ mm.}, \quad D^{23} \quad 1·472,$$

n_D^{20} 1·584.

In the case of *o*-allylphenol, it is necessary to acetylate before the bromination, because the free phenol reacts in a complicated manner with bromine. When slowly treated with bromine in carbon disulphide at 0° or below, and the product is slowly distilled in a partial vacuum, three main fractions are obtained. Fraction I, b. p. 90—125°/20 mm., is the greatest, and consists chiefly of 1-methylcoumaran, b. p. 93—94°/23 mm., D^{24} 1·032, n_D^{22} 1·531 (Claisen, A., 1913, i, 1176; 1915, i, 707). Fraction II, b. p. 125—146°/20 mm., contains two isomerides with b. p. 142°/20 mm.; one is 4-*bromo*-1-*methylcoumaran*, D^{24} 1·414, n_D^{22} 1·569, and the other is 1-bromomethylcoumaran, since it yields 1-methylenecoumaran when the mixture is boiled with alcoholic potassium hydroxide, and 1-methylcoumaran when boiled with zinc and hydrochloric acid. Fraction III, b. p. 180—210°/20 mm., contains chiefly *α*-4-*dibromo*-1-*methylcoumaran*,

$$C_6H_3Br{\textstyle<}^{CH_2}_{O-\!\!-}{\textstyle>}CH\cdot CH_2Br,$$

b. p. 189—194°/20 mm., D^{24} 1·795, n_D^{22} 1·607, for. when reduced by zinc and hydrochloric acid, it yields the above 4-bromo-1-methyl-coumaran, and when treated with alcoholic potassium hydroxide it forms 4-*bromo*-1-*methylenecoumaran*, b. p. 148°/30 mm., D^{24} 1·483, n_D^{22} 1·595.

An attempt was made to obtain *o*-$\beta\gamma$-dibromopropylphenol from its methyl ether. *o*-*Allylanisole*, b. p. 101—102°/22 mm., D^{24} 0·972, n_D^{22} 1·526, prepared by the action of methyl sulphate on *o*-allylphenol, reacts with bromine in carbon disulphide, however, to form some of the same compounds as the free phenol.

4-Bromo-2-allylphenol (Claisen, *loc. cit.*) yields the above 4-bromo-1-methylcoumaran when heated with pyridine hydro-

chloride, and this may also be obtained by brominating 1-methyl-coumaran. 4-*Bromo-2-allylphenyl benzoate* has b. p. 234—236°/25 mm., D^{24} 1·308, n_D^{22} 1·589, and its *dibromide*, m. p. 98·5°, yields the above 4-bromo-1-methylenecoumaran when boiled with alcoholic potassium hydroxide.

3-Allyl-*p*-cresol and 3-allyl-*o*-cresol (*ibid.*) give the following compounds: 3-*allyl*-p-*tolyl acetate*, b. p. 139°/22 mm., D^{20} 1·022, n_D^{20} 1·507, its *dibromide*, long, white needles, m. p. 77·5°, and 4-*methyl*-1-*methylenecoumaran*, b. p. 113°/17 mm., D^{20} 1·043, n_D^{20} 1·556; and 3-*allyl-o-tolyl acetate*, b. p. 128°/14 mm., D^{20} 1·023, n_D^{20} 1·507, its *dibromide*, b. p. 210°/20 mm., and 6-*methyl*-1-*methylenecoumaran*, b. p. 101—102°/15 mm., D^{20} 1·043, n_D^{20} 1·553.

1-Allyl-β-naphthol (Claisen, A., 1912, i, 965) forms an *acetate*, b. p. 186—189°/17 mm., D^{25} 1·111, n_D^{22} 1·584, the *dibromide* of which, fibres, m. p. 89°, yields 2-*methylene-2 : 3-dihydro-4 : 5-αβ-naphthafuran* (annexed formula), m. p. 55°, b. p. 188—190°/17 mm., when boiled with sodium ethoxide solution.
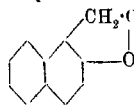
3-Allylsalicylic acid and its methyl ester (Claisen, *loc. cit.*) cannot be acetylated, but this is no hindrance to the above reaction, as the hydroxyl group needs no protection during bromination. *Methyl* 3-βγ-*dibromopropylsalicylate*, m. p. 72—72·5°, and the free *acid*, $CO_2H \cdot C_6H_3(OH) \cdot CH_2 \cdot CHBr \cdot CH_2Br$, needles, m. p. 162·5—163·5°, both yield 1-*methylenecoumaran-6-carboxylic acid*, m. p. 152°, when boiled with alcoholic potassium hydroxide, and this compound gives 1-*bromomethylenecoumaran-6-carboxylic acid*,

$$CO_2H \cdot C_6H_3 {<}^{CH_2}_{O-} {>} C{:}CHBr,$$ m. p. 222—223°, when treated with bromine in carbon disulphide at 0°.   J. C. W.

Syntheses of Chromans and Coumarans. R. E. RINDFUSZ (*J. Amer. Chem. Soc.*, 1919, **41**, 665—670).—Three simple methods for the preparation of chroman and coumaran have been discovered.   I. Phenyl γ-hydroxypropyl ether, from trimethylene-chlorohydrin and sodium phenoxide, is heated with zinc chloride, giving chroman in 30—35% yield, or phenyl β-hydroxyethyl ether, from ethylene chlorohydrin and sodium phenoxide, is similarly treated, giving a 25% yield of coumaran.   II. Phenyl γ-bromopropyl ether or phenyl β-bromoethyl ether, from sodium phenoxide and the dibromides, heated with zinc chloride, gives a 65% yield of chroman or a 30—40% yield of coumaran as the case may be.   III. Mixtures of phenol and the chlorohydrins are heated with zinc chloride, but the yields are not so good.

It is obvious that substituted chromans and coumarans could be made very readily from substituted phenols.   J. C. W.

Cinchona Alkaloids.   II.   5-Azo- and 5-Amino-compounds of Cupreine, Hydrocupreine, and their Methyl and Ethyl Ethers. G. GIEMSA and J. HALBERKANN (*Ber.*, 1919, **52**, [*B*], 906 -923.   Compare this vol., i, 33).—5-*Benzeneazocupreine*, anhy-

drous, microscopic needles, m. p. 129—130°, is obtained by the action of diazotised aniline on an alkaline solution of cupreine; the corresponding *sodium* p-*sulphonate* (from diazotised sulphanilic acid) forms ruby-red crystals ($+6H_2O$), which have m. p. 212° (decomp.) after darkening at 200°, whilst the free p-*sulphonic acid* separates from water in red, prismatic needles ($+3H_2O$), which, when dehydrated, decompose at 257° after darkening at 250°. Reduction of the azo-compounds, preferably with sodium hyposulphite in alkaline solution, leads to the formation of 5-*amino-cupreine*, an unstable, non-crystalline mass, m. p. generally between 170° and 195°, $[a]_D^{20} - 121\cdot2°$ (in ether), $[a]_D^{20} - 18\cdot4°$ (in alcohol). The salts are stable; the *platinichloride*, microcrystalline needles, decomposing at about 220°; the *monosulphate*, yellow, prismatic needles, which are completely decomposed at 232°; the *disulphate*, red prisms, which darken at about 170° and decompose above 200° (this is the most stable sulphate and separates from solutions containing more than the requisite quantity of sulphuric acid); the *trioxalate*, dull red powder, m. p. 152—153° (decomp.); and the *tetrasulphate*, colourless, microscopic needles, m. p. 187° (decomp.), after previous sintering and darkening, are described. 5-*Benzoylaminocupreine* forms a grey powder, m. p. about 135°, after previous contraction. $[a]_D^{20} + 39\cdot8°$ (in alcohol); 5-*dibenzoylaminocupreine* resembles the monobenzoyl derivative, melts indefinitely at 165°, and has $[a]_D^{20} + 41\cdot6°$ (in alcohol); *tribenzoylaminocupreine* crystallises in colourless, rhombic plates, m. p. 183°, $[a]_D^{20} + 131\cdot1°$ (in alcohol). The primary product of the interaction of 5-aminocupreine and phenylthiocarbimide in alcoholic solution appears to be the *thiocarbamide*, small, colourless needles or plates, m. p. 247° (decomp.), after much previous softening, which, however, readily loses hydrogen sulphide and forms the corresponding *carbanilide*, colourless, anhydrous needles or rods, m. p. 185—186° (from benzene), small, monohydrated needles, m. p. 155° after previous softening (from dilute alcohol). *Cupreine-5-thioloxazole*, microscopic needles which do not melt below 300°, is obtained as by-product of the action of phenylthiocarbimide on 5-aminocupreine or, more conveniently, by the direct action of carbon disulphide on the latter; it gives a *monosulphate*, red needles ($+4H_2O$), which is only stable in solution in the presence of an excess of acid.

5-*Aminoquinine*, m. p. 214—215°, $[a]_D^{20} - 22\cdot5°$ (in alcohol), -119·3° (in ether), is obtained in small yield by the methylation of 5-aminocupreine by methyl sulphate or diazomethane. 5-*Aminoethylcupreine* forms prismatic needles or plates, m. p. 213—214°, $[a]_D^{20} - 21\cdot5°$ (in alcohol), -121·6° (in ether); the *platinichloride* ($+1H_2O$), darkening at about 195° and gradually decomposing at a higher temperature; the *monosulphate*, slender needles ($+3H_2O$), m. p. 183—184° (decomp.) after darkening at 173°, and the *disulphate*, red powder, m. p. 143° (decomp.) after darkening at 100°, are described. Reduction of aminoethylcupreine with hydrogen in the presence of palladium readily yields the hydro-*base*, m. p. 212°.

Sodium hydrocupreine-5-azobenzene-p-sulphonate is obtained in the same manner as the corresponding cupreine compound, to which it shows the closest resemblance; the corresponding *sulphonic acid* ($+3H_2O$) is also described. *5-Aminohydrocupreine* is an unstable substance which darkens above 100°, softens about 160°, and has m. p. 197° (on account of incipient decomposition the latter value is seldom observed, the m. p. usually being 180—185°); it has $[a]_D^{20} -125.9°$ (in ether), $-24.0°$ (in alcohol); it gives a *monosulphate*, yellow needles, which darken at 180° and decompose without melting above 200°, and a *disulphate*, rust-red powder which decomposes above 160°. *5-Aminohydroquinine*, yellow needles, m. p. 217—218°, is obtained in the same manner as 5-amino-quinine, which it greatly resembles and from which it can be prepared by catalytic reduction; it has $[a]_D^{20} -14.1°$ (in alcohol), $-120.6°$ (in ether). *5-Aminoethylhydrocupreine* forms intensely yellow crystals, m. p. 211—212°, $[a]_D^{20} -123.8°$ (in ether), $-13.2°$ (in alcohol); when treated with ethyl chloroformate it yields amorphous ethylhydrocupreine ethyl urethane, m. p. 100—110°, $a_D^{20} +14.8°$.   H. W.

Diazo-reaction of Morphine. LUDWIG LAUTENSCHLÄGER (*Arch. Pharm.*, 1919, **257**, 13—18).—Morphine and its salts couple with diazonium compounds in alkaline solution to yield dyes, the most suitable reagent being diazobenzenesulphonic acid. For qualitative work an approximately 2% aqueous solution of the latter is added to the solution of the morphine salt which is made alkaline with sodium carbonate or hydrogen carbonate; a deep red to pale red coloration, according to the concentration of the alkaloid, is immediately developed, which becomes orange after acidification with dilute acid. The limit of sensitiveness for the sodium carbonate solution is less than 1 in 10,000. The dye has little affinity for fibres in an acid bath.

Morphine is the only member of the opium alkaloids which yields a true dye with diazonium compounds; the synthetic derivatives of morphine (dionin, heroin, peronin) do not give the reaction, whilst of the commoner pharmacological alkaloids only a few give dyes. A table is given in the original showing the colorations yielded by morphine, emetine, sparteine, physostigmine, piperidine, coniine, and nicotine with diazobenzenesulphonic acid, diazotised arsanilic acid, 2:5-dichlorobenzenediazonium chloride, *p*-nitrobenzenediazonium chloride, and benzidine tetrazotate in alkaline solution.

The constitution of the morphine dyes remains undecided, but titration with titanous chloride shows that one and two molecules of morphine are contained in the diazo- and tetrazo-dyes respectively. Methyl- and ethyl-morphine do not give the reaction. The physiological action of morphine is destroyed by its conversion into the diazonium compound. Attempts to obtain an aminomorphine by reduction of the dye under varying conditions did not lead to the desired result.

The reaction can be used for the toxicological detection of morphine in the presence of its substituents and of other alkaloids.

Quantitative determinations show that morphine can be estimated as accurately by the colorimetric method with diazobenzenesulphonic acid as by iodic acid or by Marquis's method; the method is most suitably applied to solutions containing $0.5—0.05$ mg. of alkaloid per c.c., and has the advantage that it is not influenced by the presence of other opium alkaloids. A series of estimations of morphine in ripe poppy heads by the diazo- and iodic acid methods yielded identical results.

H. W.

Oxydihydrocodeinone Hydrochloride [Eukodal]. MARTIN FREUND and EDMUND SPEYER (*Münch. med. Woch.*, 1917, **64**, 380—381; from *Chem. Zentr.*, 1919, i, 28—29).—Thebaine eliminates methyl alcohol when oxidised by hydrogen peroxide and passes into a tertiary base, $C_{18}H_{19}O_4N$, which contains only one methoxygroup and has ketonic properties; one hydrogen atom in thebaine is replaced by hydroxyl. The substance is related to codeinone, obtained by the oxidation of codeine, and, since it contains an additional atom of oxygen, is termed oxycodeinone. The aliphatic double bond in oxycodeinone is reduced by hydrogen, yielding *oxydihydrocodeinone* (annexed formula). The base crystallises in rods, m. p. $220—222°$. The hydrochloride is a stable substance, freely soluble in water. The solution can be sterilised by heat without undergoing decomposition. The free base is precipitated in the crystalline form by addition of ammonia, sodium carbonate or hydroxide, and does not dissolve in an excess of alkali. Eukodal is used as a narcotic.
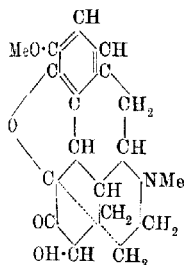
H. W.

The Alkaloids of the Pomegranate Tree. VI. The Relationship between Methyl*iso*pelletierine, *dl*-Methylconhydrinone, and *N*-Methylpiperidylpropan-α-one. An Instance of Isomerism with Substances containing an Asymmetric Tervalent Nitrogen Atom. KURT HESS (*Ber.*, 1919, **52**, [*B*], 964—1004).—It has been previously shown that methyl*iso*pelletierine is α-1-methylpiperidylpropan-α-one, and that it may be formed from conhydrine (A., 1918, i, 35); a more extended examination of the latter reaction now proves that two bases are formed, one of which is identical with methyl*iso*pelletierine, whilst the other is *dl*-methylconhydrinone. Synthesis of α-1-methylpiperidylpropan-α-one leads to a product identical with the latter. The formation of methyl*iso*pelletierine from conhydrine is, however, shown not to be due to impurity in the latter, and further confirmation of the formula ascribed to it is obtained by its oxidation to α-methyl-

p^*

piperidinecarboxylic acid and acetic acid. Since the two bases yield different oximes and hydrazones, their isomerism cannot be attributed to keto-enolic desmotropy, and the author is led to the conclusion that it is due to the presence of an asymmetric carbon atom and an asymmetric tervalent nitrogen atom in the molecule. The following formulæ are then possible:

$$
\begin{array}{cc}
\overset{+|}{COEt \cdot C \cdot H} & \overset{|+}{H \cdot C \cdot COEt} \\
+N \cdot Me & Me \cdot N \\
(\overset{|}{C}H_2)_4 & (\overset{|}{C}H_2)_4
\end{array}
\qquad
\begin{array}{cc}
\overset{+|}{COEt \cdot C \cdot H} & \overset{|+}{H \cdot C \cdot COEt} \\
Me \cdot N^+ & +N \cdot Me \\
(\overset{|}{C}H_2)_4 & (\overset{|}{C}H_2)_4
\end{array}
$$

$$\underbrace{\hspace{4cm}}_{a.}\qquad\underbrace{\hspace{4cm}}_{b.}$$
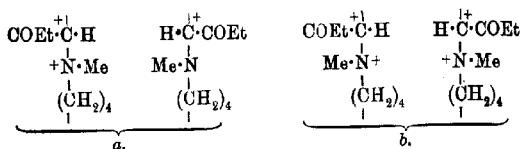
(For convenience, the piperidine ring is represented as opened at one point and placed in the plane of the paper.) Owing to the relative readiness with which methyl*iso*pelletierine reacts with semicarbazide, the formula, a, is tentatively proposed for it. Unexpectedly, the isomerism is still preserved when the bases are converted into their methiodides, although this phenomenon does not appear to have been observed previously with quaternary ammonium salts of the type [NABCC]X; a similar case may, however, be presented by Willstätter's dihydroarecoline methiodide and the methiodide of methyl methylhexahydronicotinate (Hess and Liebbrandt, this vol., i, 220).

It has not been possible, up to the present, to cause the interconversion of methyl*iso*pelletierine and *dl*-methylconhydrinone.

[With FRL. A. EICHEL.]—Methylconhydrine (A., 1918, i, 35) has $[\alpha]_D^{20} - 42 \cdot 27°$ (in water), $[\alpha]_D^{20} - 39 \cdot 42°$ (in alcohol). *d*-Conhydrinone (*loc. cit.*) has $[\alpha]_D^{20} - 11 \cdot 42°$ in aqueous solution; it gives a *hydrobromide*, m. p. 146° after previous softening, a *picrate*, m. p. 91—92°, an *ethylurethane*, b. p. 133°/15 mm., and an impure *hydrazone*, b. p. 123—125°/18 mm., which yields a *picrate*, m. p. 164° after previous softening. Methylation of *d*-conhydrinone with methyl sulphate in the presence of alkali leads to a mixture of racemic methylconhydrinone and methyl*iso*pelletierine, the ultimate separation of which is accomplished by taking advantage of the fact that the latter readily reacts with semicarbazide, to which the former is indifferent. *dl-Methylconhydrinone* is a colourless oil, b. p. 95°/15 mm.; it gives a *hydrochloride*, needles, m. p. 124° after softening from 119°, a *picrate*, cubic crystals, m. p. 106°, a *hydrobromide*, slender needles, m. p. 137—138° after previous softening, and an oily *oxime*, b. p. 158°/22 mm., which yields a *picrate* melting to a cloudy liquid at 118° and becoming transparent at about 145°. When *d*-conhydrinone is treated with methyl iodide, the *methiodide* of the tertiary base is produced; it forms prisms, m. p. 113°, $[\alpha]_D^{15} - 2 \cdot 47°$.

Attempts to methylate or oxidise ψ-conhydrine, under conditions which were found suitable for conhydrine, did not lead to a satisfactory result, the material being recovered unchanged.

[With H. MUNDERLOH.]—α-1-Piperidylpropan-α-ol is prepared by the catalytic reduction of α-ethylpyridyl ketone, and is obtained in two forms, m. p.'s 99—100° and 83—85° respectively, which, on methylation, yield α-1-*methylpiperidylpropan-α-ols*, b. p.'s 96—97°/ 14 mm. and 97—99°/1 mm. respectively. Oxidation of a mixture of the latter substances gives α-1-*methylpiperidylpropan-α-one*, b. p. 88—89°/12 mm., which is shown to be identical with *dl*-methylconhydrinone by an exhaustive examination of the picrate, hydrochloride, hydrobromide, and methiodide.

For purposes of comparison, a number of derivatives of methyl-*iso*pelletierine has been prepared. The *hydrochloride* of the *dl*-base has m. p. 156° and decomposes at 160°; the *methiodide* forms cubic crystals, m. p. 156°; the *oxime* is a viscous oil, b. p. 160°/12 mm., which forms a *picrate* (or possibly mixture of picrates), m. p. 106°; the *methiodides* of the *d*- and *l*-bases also have m. p. 156°, but depression of the melting point is observed when they are mixed with the racemic form.

Methyl*iso*pelletierine is oxidised by chromic acid in sulphuric acid solution to *methyliso*pelletierinic *acid*, which is shown to be identical with 1-methylpiperidine-2-carboxylic acid previously synthesised by Hess and Liebbrandt (A., 1917, i, 354) in the form of its ethyl ester; the air-dried acid $(+\frac{1}{2}H_2O)$ has m. p. 214—215° [*hydrochloride*, m. p. 205°; *platinichloride* $(+2H_2O)$, m. p. 218—219° (decomp.)]; the *methiodide* of the ethyl ester crystallises in short rods, m. p. 129—131°; the *gold* salt of the methochlorides of the ethyl ester and of the acid have m. p.'s 88° and 254° (decomp.) respectively. The methiodide of ethyl 1-methylpipecolinate and some of its derivatives have previously been described by Willstätter; repetition of his work has, however, yielded products identical with those obtained from methyl*iso*pelletierine and differing in their physical constants from those described by him.

Attempts to demethylate methyl*iso*pelletierine by cyanogen bromide yielded *methyliso*pelletierine *methobromide*, m. p. 134—136°, and the expected cyanamide *derivative*, b. p. 173°/ 14 mm.; hydrolysis of the latter gave an iminazolone *derivative*, probably annexed formula. The *imino-ketone*, b. p. 101—102°/14 mm., could, however, be obtained by treatment of methyl*iso*pelletierine with ethyl azodicarboxylate; it gives a *picrate*, m. p. 154°, a *hydrobromide*, slender needles, m. p. 149°, and a *hydrochloride*, m. p. 137—138°, after previous softening.
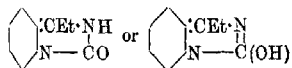
*iso*Pelletierine is not methylated by formaldehyde and formic acid, but is converted by methyl sulphate into methyl*iso*pelletierine; *dl*-methylconhydrinone does not appear to be formed in this reaction. Attempts to convert methyl*iso*pelletierine into *dl*-methylconhydrinone by treatment with acetic and hydrochloric acids at 200°, with glacial acetic acid at 110—120°, with alcohol at 105—115°

or with alcoholic sodium ethoxide solution yielded only unchanged
material and resinous or oily products.   H. W.

**The Alkaloids of the Pomegranate Tree. VII.   Natural
Occurrence of isoPelletierine.**   KURT HESS (*Ber.*, 1919, **52**, [*B*],
1005—1013).—During the preparation of the large quantities of
alkaloids required in the investigation of methyl*iso*pelletierine (pre-
ceding abstract), the author has observed the occur-
rence of *iso*pelletierine (annexed formula) in small
amount.   The alkaloids are separated in much the
same manner as previously described; after removal
of ψ-pelletierine by freezing, and of the bulk of pelle-
tierine as the hydrobromide, the residual material
is distilled under diminished pressure, when considerable quantities
of resin are left behind.   The distillate is treated with ethyl
chloroformate, and the product is repeatedly fractionated, when,
after removal of α-1-methylpiperidylpropan-β-one and methyl*iso*-
pelletierine, a small fraction is obtained, b. p. 150—165°/13 mm.,
which consists of a mixture of the urethanes of pelletierine and
*iso*pelletierine.   When hydrolysed with aqueous-alcoholic sodium
hydroxide solution, the liberated pelletierine is resinified (the pre-
parative regeneration of pelletierine from its urethane cannot be
accomplished at present in spite of many variations in the condi-
tions of the experiments), whilst the *iso*pelletierine is unaffected
and is obtained on distillation as an optically-inactive oil, b. p.
102—107°/11 mm.   The picrate has m. p. 152° after previous
softening, whereas that obtained from *iso*pelletierine formed by
demethylation of methyl*iso*pelletierine (preceding abstract) has
m. p. 154° after previous softening; mixed m. p. 154°.   The hydro-
bromides of the natural and synthetic bases and mixture of them
melt at 149°.

The yields of the various alkaloids from 100 kilos. of the bark
are approximately as follows: pelletierine, 52·5 grams; ψ-pelle-
tierine, 179 grams; methyl*iso*pelletierine, 22 grams; *iso*pelle-
tierine, about 1·5 grams; α-1-methylpiperidylpropan-β-one, about
1 gram.

Owing to an error in calculation, the specific rotations of a
number of salts of pelletierine and methyl*iso*pelletierine are incor-
rectly recorded in a previous paper (A., 1918, i, 404); the following
are the accurate values: *d*-Pelletierine *d*-bitartrate, $[\alpha]^{20} + 21·00°$;
$[\alpha]^{21} + 20·93°$; *l*-pelletierine *l*-bitartrate, $[\alpha]^{20} - 20·94°$, $[\alpha]^{21}$
$-21·80°$; *d*-pelletierine sulphate, $[\alpha]^{18} + 5·86°$, $+ 6·11°$; *l*-pelle-
tierine sulphate, $[\alpha]^{18} - 5·89°$; *d*-methyl*iso*pelletierine *d*-bitartrate,
$[\alpha]^{20} + 22·77°$; *l*-methyl*iso*pelletierine *l*-bitartrate, $[\alpha]^{18} - 20·83°$ and
$-22·40°$; *d*-methyl*iso*pelletierine sulphate, $[\alpha]^{18} + 7·64°$, 8·53°;
l-methyl*iso*pelletierine sulphate, $-8·03°$; *d*-methyl*iso*pelletierine
hydrochloride, $[\alpha]^{18} + 11·08°$; *l*-methyl*iso*pelletierine hydrochloride,
$[\alpha]^{18} - 10·64°$.   H. W.

Some Derivatives of Piperonaldehyde.   RUDOLF WILKENDORF
(*Ber.*, 1919, **52**, [*B*], 606—616).—I. *Quinazoline derivatives.—*

Piperonaldehyde is nitrated by dropping a concentrated acetic acid solution into well-cooled and agitated nitric acid (D 1·41), and then converted further into the oxime and reduced to *o*-aminopiperon-aldoxime (Haber, A., 1891, 704). This is reduced by means of sodium amalgam and alcohol, the solution being maintained slightly acid by the addition of acetic acid, when 6-*amino*-3:4-*methylene-dioxybenzylamine* is obtained as an oily base, which forms a *dihydrochloride*, bundles of long, sharp needles, decomp. 175—180°, and a yellow *mono-picrate*. When heated with sodium formate and anhydrous formic acid, the salt produces 6:7-*methylenedioxy*-3 : 4-*dihydroquinazoline*, $CH_2:O_2:C_6H_2\!\!<^{CH_2\cdot NH}_{N=\!\!=CH}$, which crystallises in bitter needles, m. p. 153°, and forms a *hydro-chloride*, bundles of needles, m. p. 267—268° (decomp.), an almost insoluble *picrate*, m. p. 234°, and an insoluble *platinichloride*, decomp. 235°. When oxidised by alkaline ferricyanide, the base yields 6:7-*methylenedioxyquinazoline*, m. p. 172—173° (after vacuum distillation), which gives a *picrate*, long, slender, pale yellow needles, m. p. 216°, and a *platinichloride*, decomp. 270—275°, and may be reduced by sodium amalgam to 6:7-*methylenedioxy*-1:2:3:4-*tetrahydroquinazoline*. This crystallises in glossy leaflets, m. p. 101°, and forms a *picrate*, terra-cotta-coloured tablets, m. p. 172—173° (decomp.).

The original base forms a *triacetyl* derivative, $C_7H_7N_2Ac(OAc)_2$ or $C_7H_6N_2Ac_2(OAc)\cdot OH$, bundles of slender needles, m. p. 200—201°, when shaken with acetic anhydride in the cold, but the *benzoyl* derivative, $CH_2:O_2:C_6H_2(NH_2)\cdot CH_2\cdot NHBz$, m. p. 255°, is obtained by the Schotten-Baumann method.

II. 6-*Nitropiperonyl Alcohol*.—6-Nitropiperonyl chloride (Robin-son and Robinson, A., 1916, i, 167) does not react at all readily with potassium carbonate solution, and was therefore converted by means of sodium iodide into the *iodide*,

$$CH_2:O_2:C_6H_2(NO_2)\cdot CH_2I.$$
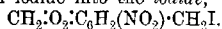
This crystallises in bundles of elongated, pale yellow needles, m. p. 97—98°, but it does not irritate the skin, as the chloride does, and fails to react with silver oxide. With the idea that the iodine atom may have wandered into a ring position, the substance was chlorinated, in the expectation that a compound of the type $R\cdot ICl_2$ would be formed. During the process, however, iodine is liberated, and ultimately a *dichloro*-6-*nitropiperonyl chloride* is formed, either $CH_2:O_2:C_6Cl_2(NO_2)\cdot CH_2Cl$ or

$$CCl_2:O_2:C_6H_2(NO_2)\cdot CH_2Cl,$$
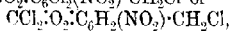
pale yellow needles, m. p. 139—140°. Both the chloride and the iodide react readily with sodium acetate in alcoholic solution to form the *acetate*, tablets, m. p. 150°, which may be hydrolysed by boiling with 20% sulphuric acid to 6-*nitropiperonyl alcohol* [6-*nitro*-3:4-*methylenedioxybenzyl alcohol*],

$$CH_2:O_2:C_6H_2(NO_2)\cdot CH_2\cdot OH,$$
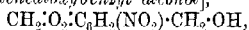
this forming pale yellow crystals, m. p. 121°. The corresponding *thiocyanate*, m. p. 88—89°, is obtained by the action of potassium

thiocyanate on the chloride in boiling alcohol, and may be converted by treatment with ammonium sulphide into *di-6-nitro-piperonyl disulphide*, $[CH_2:O_2:C_6H_2(NO_2)\cdot CH_2]_2S_2$, pale yellow needles, m. p. 103—104°.   •   J. C. W.

Formation and Reactions of Imino-compounds. XIX. The Chemistry of the Cyano-acetamide and Guareschi Condensations. GEORGE ARMAND ROBERT KON and JOCELYN FIELD THORPE (T., 1919, 115, 686—704).

Nitration of Diphenylethylenediamine. GEORGE MACDONALD BENNETT (T., 1919, 115, 576—578).

New Derivatives in the Indole and Indigotin Groups. Isatin. III. AUGUST ALBERT and LEOPOLD HURTZIG (*Ber.*, 1919, 52, [*B*], 530—542. Compare A., 1915, i, 595; this vol., i, 99).— In the last paper, the behaviour of 1-oxy-2-thiol-3-benzoyloxy-3-hydroindole towards phenylhydrazine, and various reactions of the product, were described. Similar experiments with β-naphthyl-hydrazine are now recorded.   •

o-Nitrobenzaldehyde is converted into its cyanohydrin, from which the required material is obtained by benzoylating and then reducing with ammonium sulphide and shaking the thioamide with dilute hydrochloric acid. 2-*Thiol*-3-*benzoyloxy*-1 : 3-*dihydroindole*--1-β-*naphthylhydrazone hydrate*,

$$C_{10}H_7\cdot NH\cdot NH\cdot N(OH){\Large<}^{C_6H_4}_{C(SH)}{\Large>}CH\cdot OBz,$$
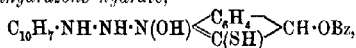
forms colourless needles, m. p. 120—122° (fuses to a red liquid), and reacts with 0·5*N*-sodium hydroxide to give 1 : 1′-*bis*-β-*naphthyl-hydrazinoindigotin*, which crystallises in dark red, lanceolate needles, m. p. 228° (decomp.), gives a brown sulphate which is easily hydrolysed, and changes into the bluish-red salt of the enolic form when covered with concentrated sodium hydroxide. The presence of two carbonyl groups is revealed by the formation of a *bisphenylhydrazone*, bundles of pale yellow needles, m. p. 183°, and the *dihydrochloride* of a *di-anil*, wine-red needles, m. p. 202°. The N : N′-*dibenzoyl* derivative,

$$C_6H_4{\Large<}^{CO\text{———}}_{N(NH\cdot NBz\cdot C_{10}H_7)}{\Large>}C{:}C{\Large<}^{CO\text{———}}_{N(NH\cdot NBz\cdot C_{10}H_7)}{\Large>}C_6H_4,$$
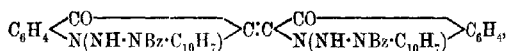
is obtained by boiling the indigotin with 10*N*-sodium hydroxide until it is completely changed into a bluish-red powder, and then shaking with benzoyl chloride in the cold; it forms sharp, yellow needles, m. p. 184°, and gives a yellow *bisphenylhydrazone*, $C_{82}H_{46}O_2N_{10},2H_2O$, m. p. 140—142° (after some decomposition at 107°). A *tetrabenzoyl* derivative,

$$C_6H_4{\Large<}^{C(OBz)\text{———}}_{N(:N\cdot NBz\cdot C_{10}H_7)}{\Large>}C{:}C{\Large<}^{C(OBz)\text{———}}_{N(:N\cdot NBz\cdot C_{10}H_7)}{\Large>}C_6H_4,$$
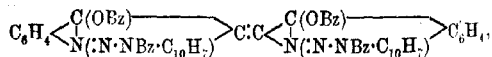
is formed if an excess of benzoyl chloride is employed; it crystal-

lises in red needles, m. p. 166°, and gives the above phenylhydrazone of the dibenzoyl derivative when warmed with phenylhydrazine.

1 : 1′-Bis-β-naphthylhydrazinoindigotin suffers reduction by ammonium sulphide to indigotin, and by zinc dust and sodium hydroxide to 1 : 1′-diaminoindigotin, which is readily converted into indigotin-1 : 1′-imide. The acetyl derivative of this crystallises in bluish-violet needles, m. p. 212° (*loc. cit.*), and the oxime fuses and resolidifies at 290°. Reduction with zinc and acetic acid gives β-naphthylamine and the lactim form of isatin, for phenylhydrazine precipitates the α-phenylhydrazone, $C_6H_4\!\!<\!\!^{CO}_{NH}\!\!>\!\!C\!:\!N\!\cdot\!NHPh$

(Heller, A., 1907, i, 442). J. C. W.

Preparation of Hydantoins. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 309508; from *Chem. Zentr.*, 1919, ii, 262).—The method depends on the action of hypohalogenites on C-C-arylalkylcyanoacetamides. Thus, the sodium compound of phenylcyanoacetamide reacts with ethyl iodide to form *phenylethylcyanoacetamide*, crystals, m. p. 116°, which is dissolved by sodium hypobromite solution and yields, after short warming, *phenylethylhydantoin*, small, shining needles, m. p. 201—202°. Phenylallylhydantoin is similarly prepared. The arylalkylhydantoins are useful soporifics. H. W.

Preparation of Hydantoins. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 310426, additional to D.R.-P. 309508; from *Chem. Zentr.*, 1919, ii, 262. Compare preceding abstract).—The preparation is effected by the action of hypohalogenites on malonamide. Thus, diethylmalonamide and potassium hypobromite yield diethylhydantoin. *Phenylethylmalonamide*, prepared from phenylethylcyanoacetamide and concentrated sulphuric acid at 125°, forms small leaflets, m. p. 124° (decomp.), and is converted by sodium hypobromite after some hours into phenylethylhydantoin, m. p. 201°; if the solution is acidified immediately after solution of the amide, a chlorinated *amide*,

$$NH_2\!\cdot\!CO\!\cdot\!CEt_2\!\cdot\!CO\!\cdot\!NHCl,$$
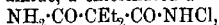
colourless needles, m. p. 152°, is obtained when hypochlorite is used. Diallylmalonamide yields C-C-*diallylhydantoin*, colourless needles, m. p. 204°. H. W.

Reduction of the Nitrile Group. J. J. BLOCH (*J. Soc. Chem. Ind.*, 1919, **38**, 118—120).—The author describes a series of unsuccessful attempts to reduce the nitrile group in 5-cyanomethylbenziminazole and 5-cyanomethyl-2-methylbenziminazole (Maron, Kontorowitsch, and Bloch, A., 1914, i, 684) to the amino-group. With sodium and alcohol, reduction proceeds mainly according to the scheme : $R\!\cdot\!CH_2\!\cdot\!CN + Na + H = R\!\cdot\!CH_3 + NaCN$; with palladium hydrosol, with acetic acid and iron, sodium amalgam, aluminium amalgam, or zinc dust, only traces of base are obtained. The use of mineral acids causes hydrolysis of the nitrile. 2-*Methyl-*

iminazolylphenylacetic acid, $CO_2H \cdot CH_2 \cdot C_6H_3 \overset{\cdots N}{\underset{NH}{\diagdown}}\!\!\!\gg\!\! CMe$, has
m. p. 218—219° (anhydrous), 117° ($+2H_2O$); the *mercuric* salt
decomposes without melting at 230°.

Reduction of benzyl cyanide with sodium and alcohol gives
phenylethylamine in 35—40% yield, the process being improved
by the addition of toluene. Toluene, ammonia, methylamine, and
sodium cyanide are always formed, the two main reactions being
the normal reduction to the amine, and $CH_2Ph \cdot CN + Na + H \longrightarrow$
$PhCH_3 + NaCN$ (compare Johnson and Guest, A., 1909, i, 784).

H. W.

Improvements in the Production of a Colouring Matter
(*N*-Dihydro-1 : 2 : 2′ : 1′-anthraquinone-azine). JAMES MORTON,
ARTHUR GILBERT DANDRIDGE, and MORTON SUNDOUR FABRICS, LTD.
(Brit. Pat., 126112).—The substitution of potassium chlorate for
potassium nitrate in the preparation of *N*-dihydro-1 : 2 : 2′ : 1′-
anthraquinone-azine from 2-aminoanthraquinone by fusion at 250°
with potassium hydroxide and an oxidising agent (see Brit. Pats.,
3239, 22762 of 1901) results in an improved yield of dye of much
greater purity, which dyes cotton to much brighter shades than
can be obtained with the impure dye prepared by the older method.
[See, further, *J. Soc. Chem. Ind.*, 1919, July.]   G. F. M.

Structure of Hydroxyquinacridone. WL. BACZYŃSKI and
ST. VON NIEMENTOWSKI (*Ber.*, 1919, **52**, [*B*], 461—484. Compare
A., 1896, i, 261).—The hydroxyquinacridone obtained by the con-
densation of anthranilic acid with phloroglucinol might have either
a linear structure like anthracene or an angular structure like
phenanthrene. Decisive evidence has been very hard to find, but
the authors are now able to show that the annexed, angular, or
"β" structure is correct, which is in keeping with the results of
many other syntheses of quinoline derivatives
with at least three nuclei.
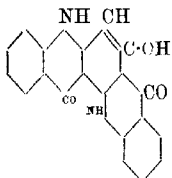
In the first place, the condensation product
of phloroglucinol with *o*-aminobenzaldehyde
was shown to be 4-hydroxy-β-quinacridine,
because it could be oxidised to a diketone
which condensed with *o*-phenylenediamine, and
was therefore an *o*-diketone. Similarly,
hydroxyquinacridone may be oxidised by boil-
ing with chromic and acetic acids, or 6% nitric
acid, to *diketo-β-quinacridone*,

$$C_6H_4 \overset{NH \cdot C \cdot CO \cdot CO \cdot C - CO}{\underset{CO - C \quad\quad\quad C \cdot NH}{\diagdown\diagup}} C_6H_4,$$
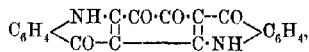
which is a microcrystalline, red powder, m. p. 374° (decomp.),
sparingly soluble in boiling quinoline or nitrobenzene, freely soluble
in concentrated sulphuric acid, from which it may be precipitated
again by dilution, otherwise insoluble. Unfortunately, it does

not react in the desired way with *o*-phenylenediamine, this reagent usually causing reduction to dihydroxy-β-quinacridone (see below). It does react with aniline, however, giving two *anils*, $C_{26}H_{15}O_3N_3,3H_2O$, one soluble in ethyl acetate, forming almost black crystals, m. p. 210—230°, and an insoluble one, also black, m. p. 320°.

Oxidation with nitric acid was then tried, with the idea of obtaining recognisable degradation products, but the results were confused by the readiness with which nitration takes place. Boiling the original compound with an acid of D 1·2 gives an 80% yield of a *nitrohydroxy-β-quinacridone*, crystallising from boiling nitrobenzene in chestnut-brown needles, m. p. 330°. If the diketone is boiled with an acid of D 1·12, it gives a *nitrodiketo-β-quinacridone*, which is best obtained from the above nitrohydroxy-compound by oxidation with chromic acid; it crystallises from nitrobenzene in yellow filaments, m. p. 340° (decomp.). A *dinitro-diketo-β-quinacridone*, $C_{20}H_8O_8N_4,H_2O$, orange leaflets, m. p. 200°, is obtained if the diketo-compound is boiled with an acid of D 1·2. When the hydroxyquinacridone is boiled with 6% nitric acid (D 1·033), the main product is the diketo-derivative (above), but small quantities of a dibasic acid are formed as well. This gives the fluorescein reaction with resorcinol, and is therefore an *o*-dicarboxylic acid, formed by the destruction of one of the outside rings. *Benzo-m-phenanthrolindicarboxylic acid*, as it is called,

$$C_6H_4\begin{matrix}NH\cdot C\cdot CH\vcentcolon C(OH)\cdot C\cdot CO-C\cdot CO_2H\\CO-C\overline{}C\cdot NH\cdot C\cdot CO_2H\end{matrix}\quad or$$

$$\begin{matrix}CO_2H\cdot C\cdot NH\cdot C\cdot CH\vcentcolon C(OH)\cdot C-CO\\CO_2H\cdot C-CO-C\overline{}C\cdot NH\end{matrix}\!\!>\!\!C_6H_4,$$
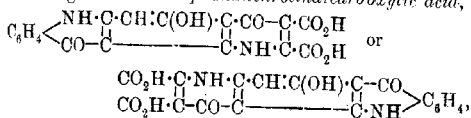
crystallises from acetone in pale yellow needles, m. p. 283° (decomp.), forms a *silver* salt, H_2O, a pale yellow *barium* salt, $3H_2O$, and a dark brown *compound*, decomp. 160—170°, of the formula, $\begin{matrix}CO\cdot C_{16}H_8O_3N_2\\O-C[C_6H_3(OH)_2]_2\end{matrix}$, when fused with resorcinol.

Better results in the oxidative degradation of the compound were obtained with permanganate. If the hydroxyquinacridone is suspended in water and gradually mixed with a saturated solution of permanganate, it is oxidised to a dibasic acid, *quinacridonic acid*, $C_6H_4\begin{matrix}NH\cdot C\cdot CO_2H\ \ CO_2H\cdot C-CO\\CO-C\overline{}C\cdot NH\end{matrix}\!\!>\!\!C_6H_4$ (or its tautomeride), which is a white, microcrystalline powder, becoming orange at 240—255°, soft at 375°, and molten at 385°. It forms an *ammonium* salt, a *barium* salt, $3H_2O$, an *ethyl hydrogen* salt, almost white nodules, m. p. 240° (decomp.), an *ethyl* ester, canary-yellow, hexagonal tablets, m. p. 417° (corr.), and an *anhydride* (by heating at 300°), crystallising in tufts of white needles, m. p. 437° (decomp.). When heated with hydrochloric acid in a sealed tube, it yields 4 : 4′-*dihydroxy-3 : 2′-diquinolyl*, in very slender needles, m. p. 430°, which dissolves in ammonia and alkali hydr-

oxide solutions with intense blue fluorescence, and is also soluble in the more concentrated solutions of hydrochloric acid. The *potassium* salt, $6H_2O$, is obtained when a solution containing 1 part in 120 parts of boiling 20% potassium hydroxide is cooled. The chief evidence in the whole argument is the fact that this dihydroxy-compound or the quinacridonic acid yields the known
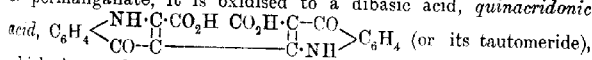
3 : 2'-diquinolyl, $C_6H_4 \underset{CH:C---C==N}{\overset{N=CH \quad CH:CH}{<}} > C_6H_4$, when distilled with

zinc dust.

The manganese dioxide sludge obtained in the oxidation of the hydroxyquinacridone with permanganate contains unchanged material and the diketoquinacridone. The latter is easily reduced by sulphurous acid in this condition (not so when previously isolated and dried), and the *dihydroxy-β-quinacridone* so formed can be extracted with alcoholic potassium hydroxide; it crystallises in brownish-yellow granules, decomp. 425°.

Various products are obtained by the action of potassium hydroxide on 4:5-diketo-β-quinacridone. Boiling with alcoholic solutions gives quinacridonic acid; prolonged boiling with 2·5% aqueous solutions produces the pale yellow *diquinolonyleneglycollic acid*,

$C_6H_4 \underset{CO--C--------C\cdot NH}{\overset{NH\cdot C\cdot C(OH)(CO_2H)\cdot C--CO}{<}} > C_6H_4$, which loses carbon

dioxide on heating and changes into *diquinolonylenecarbinol*, orange-red needles, m. p. 456—459° (*potassium* salt, red needles, with $2H_2O$). J. C. W.

Syntheses of 1 : 3-Dihydroxybenzo-2 : 5-naphthyridine [1 : 3-Dihydroxy-2 : 5-naphthadiazine] and a New Angular System of Five Nuclei, namely, Diquinopyridone. St. von Niementowski and Ed. Sucharda (*Ber.*, 1919, **52**, [*B*], 484—492). —The condensation of *o*-aminobenzaldehyde with 2:4:6-trihydroxypyridine or glutazine differs somewhat from the reaction given by anthranilic acid (A., 1917, i, 477). Besides the expected 1:3-dihydroxy-2:5-naphthadiazine (I), there is also formed a new pentacyclic compound, "diquinopyridone" (II). The former is
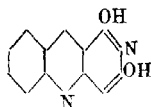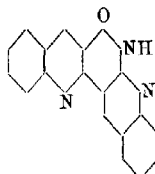
(I.)   (II.)

practically insoluble in glacial acetic acid, but readily soluble in alkali hydroxides, whereas conditions are reversed in the case of the second compound.

1 : 3-*Dihydroxy-2 : 5-naphthadiazine* (called "1 : 3-dihydroxybenzo-2 : 5-naphthyridine") crystallises in scarlet, needle-like aggre-

gates of small prisms, m. p. 375° (decomp.), and forms a yellow *hydrochloride*, 0·5H$_2$O, a mono-*acetyl* derivative, glistening, golden-yellow, rectangular plates, m. p. 350° (decomp.), a mono-*benzoyl* derivative, very thin, long, golden-yellow needles, with 1AcOH, m. p. 295° (decomp.), and a *p-nitrobenzeneazo*-compound, brownish-yellow needles, m. p. 360° (decomp.). It is decomposed by heating with hydrochloric acid in a sealed tube into 2-methylquinoline and 2-methylquinoline-3-carboxylic acid, and by boiling with 25% sodium hydroxide into 3-carboxyquinolyl-2-acetic acid (?),

$$CO_2H \cdot C_9H_5N \cdot CH_2 \cdot CO_2H.$$

Because of its deep red colour and its behaviour towards acyl chlorides and hydrolytic agents, the compound may probably have a quinonoid configuration (annexed formula).

Diquinopyridone (II) crystallises in pale straw-yellow needles, m. p. 312—314°, and forms a *dihydrochloride*, but no acyl derivatives.

J. C. W.

Vat-like Reduction Products of the Triphenylmethane Dyes. HEINRICH WIELAND (*Ber.*, 1919, **52**, [*B*], 886—886. Compare this vol., i, 99).

—The basic triphenylmethane dyes are readily reduced by sodium hyposulphite in aqueous-alkaline solution to colourless salts, which are re-oxidised to the dyes with extraordinary rapidity by air; the property is shared by the acid dyes such as aurin, the phthaleins, and fluorescein, which, however, are somewhat more slowly attacked by the alkaline reducing agent. The pure *sodium* salts have been isolated in the cases of crystalviolet and malachite-green, and appear to be derived from the triarylmethanesulphinic acids or the isomeric sulphoxylic esters; apparently, the first stage of the reaction consists in the addition of ·SO$_2$Na groups at either end of the quinonoid system, followed by the elimination of sulphur dioxide and sodium chloride. When the sulphinates are heated with an excess of alkali, the solutions lose their autoxidisability; in the case of the basic dyes, the leuco-base is precipitated, whilst the solution derived from the acid dyes contains the leuco-compound. The sulphinic group is eliminated as sulphite. The course of the autoxidation has not been definitely elucidated; the main portion of the sulphoxyl group is removed as sulphite, and the precipitate which is formed contains considerable quantities of carbinol, which, however, is not a primary product of the change.

H. W.

Pyrimidines. ADELHEID VON MERKATZ (*Ber.*, 1919, **52**, [*B*], 869—880).

—2:4:6-*Trichloro-5-ethylpyrimidine*, plates or long rods, m. p. 75—77°, is prepared by the action of phosphoryl chloride on *sodium ethylbarbiturate* (+2H$_2$O from aqueous solution); it is converted by concentrated alcoholic ammonia at the ordinary temperature into 2:6-*dichloro-4-amino-5-ethylpyrimidine*, needles, m. p. 214—216°. Fuming hydriodic acid reduces the

latter substance to 6-*iodo*-4-*amino*-5-*ethylpyrimidine hydriodide*, m. p. 204—206°. The corresponding *base* forms small needles, m. p. 191—193°, and yields a crystalline *hydrochloride*, *platini-chloride*, and *aurichloride*; when treated with zinc dust and water, it gives the *zinc double* salt of 4-amino-5-ethylpyrimidine, needles, m. p. 233—235°; the free *base* has m. p. 163° and yields crystalline *auri-* and *platini-chlorides*. The presence of the amino-group in position "4" in the pyrimidine ring follows from the non-identity of the compound with 4 : 6-*dichloro*-2-*amino*-5-*ethyl-pyrimidine*, which is synthesised in the following manner. Guanidine is condensed with ethyl ethylmalonate to form 2-*amino*-4 : 6-*dihydroxy*-5-*ethylpyrimidine*, which is converted by phosphoryl chloride into 4 : 6-*dichloro*-2-*amino*-5-*ethylpyrimidine*, needles, m. p. 191—192°; the latter is reduced by zinc dust to 2-*amino*-5-*ethyl-pyrimidine*, m. p. 142—143°, which forms double salts with mercuric, gold, and platinic chlorides. 6-*Chloro*-2 : 4-*diamino*-5-*ethylpyrimidine* is prepared by the action of alcoholic ammonia on 2 : 4 : 6-trichloro-5-ethylpyrimidine or 4 : 6-dichloro-2-amino-5-ethylpyrimidine; it forms plates, m. p. 183° (the *hydrochloride*, needles, the *platinichloride*, yellow octahedra, and the *picrate* are described), and is reduced by hydriodic acid and phosphorus to 2 : 4-*diamino*-5-*ethylpyrimidine*, m. p. 149—151°. 4 : 6-*Diamino*-5-*ethylpyrimidine* forms double pyramids, m. p. 233—235°; the *hydrochloride*, *nitrate*, long needles, *aurichloride*, small, yellow needles, and *platinichloride*, yellow rods, are described. 2 : 4 : 6-Triamino-5-ethylpyrimidine, m. p. 190° (corr.), is obtained from 2 : 4 : 6-trichloro-5-ethylpyrimidine and alcoholic ammonia at 210°, and is most readily purified by means of the *nitrate*; it separates from water +1H$_2$O, gives a readily soluble *hydrochloride*, C$_6$H$_{11}$N$_5$,2HCl, a *platinichloride*, yellow needles, an *aurichloride*, minute needles, and a crystalline *picrate*.

The action of an alcoholic solution of sodium methoxide on 2 : 4 : 6-trichloro-5-ethylpyrimidine leads to the successive replacement of the three chlorine atoms by the methoxy-group, whereby (probably) 2 : 6-*dichloro*-4-*methoxy*-5-*ethylpyrimidine*, small needles, m. p. 55—57°, 6-*chloro*-2 : 4-*dimethoxy*-5-*ethylpyrimidine*, long, colourless needles, m. p. 33—34°, and 2 : 4 : 6-*trimethoxy*-5-*ethyl-pyrimidine*, slender needles, m. p. 67—68° (crystalline salts with gold, platinic, and mercuric chlorides), are formed. The constitution of the second of these substances follows from its reduction to 2 : 4-*dimethoxy*-5-*ethylpyrimidine*, b. p. 234—236° (corr.) (the aurichloride and platinichloride salts are crystalline), and demethylation of the latter to 5-ethyluracil, m. p. 300—303° (decomp.).

Attempts to prepare derivatives of 4-phenyl-6-methylpyrimidine by the condensation of benzoylacetone with carbamide did not lead to the desired result; by using thiocarbamide, however, the thiol-pyrimidine was readily prepared, in which the mercapto-group was replaced by the hydroxy-group by treatment with dilute aqueous-chloroacetic acid solution in accordance with the directions of Wheeler and Liddle (A., 1908, i, 692); it is interesting to note

that the thioglycollates, assumed by these authors to be formed as intermediate products, are actually isolated in the present instance. *2-Thiol-4-phenyl-6-methylpyrimidine* forms amber-coloured rhombs, m. p. 199—200°; *4-phenyl-6-methylpyrimidine-2-thioglycollate* has m. p. 85°; *2-hydroxy-4-phenyl-6-methylpyrimidine* crystallises in yellow needles, m. p. 228—229° (*hydrochloride*, long needles; *picrate*, crystalline aggregates; *platinichloride*, granular; *aurichloride*, small needles). *2-Chloro-4-phenyl-6-methylpyrimidine* has m. p. 50—51° (*hydrochloride*, colourless needles); it is reduced by hydriodic acid and red phosphorus to *4-phenyl-6-methylpyrimidine*, m. p. 44—45° (*hydriodide*, yellow crystals; the *aurichloride*, *platinichloride*, and *picrate* are crystalline). H. W.

Condensation of 1-Phenyl-3-methylpyrazol-5-one with Anhydrides. SARAT CHANDRA CHATTERJEE and ANANDA KISHORE DAS (*J. Amer. Chem. Soc.*, 1919, **41**, 707—709).—Antipyrine condenses with phthalic anhydride (2 mols. to 1) at 180° to form a *compound* of the annexed formula, which crystallises in bright red needles, m. p. 212°. Succinic anhydride at 165° gives a similar *compound*, m. p. 184°. Benzoic and camphoric anhydrides give no definite products.

$$C_6H_4{<}^{CO}_{C}{>}O$$

$$\begin{array}{c}NPh\cdot CO\\N{=}CMe\end{array}{>}CH \quad CH{<}^{CO--NPh}_{CMe:N}$$

J. C. W.

Condensation Products from Amine Salts, Formaldehyde, and Antipyrine. C. MANNICH and B. KATHER (*Arch. Pharm.*, 1919, **257**, 18—33. Compare Mannich and Krösche, A., 1913, i, 101).—Antipyrine and formaldehyde react readily with the salts of secondary and primary, but not of tertiary, amines in aqueous solution, forming salts in which the hydrogen atom attached to the 4C-atom of antipyrine is replaced by the methyl group. (For the radicle, $-CH_2\cdot C_{11}H_{11}ON_2$, the nomenclature antipyrinomethyl- is proposed.) Direct condensation between formaldehyde and antipyrine can frequently be completely prevented or hindered by addition of a small quantity of pyramidone to the mixture. The substances behave similarly to those obtained from ammonium chloride, and are decomposed into the constituents by sulphurous acid. The new bases are somewhat closely allied to pyramidone, but, however, do not show any antipyretic action. Their formation appears to depend on the mobility of the hydrogen atom influenced in antipyrine by the proximity of the double bond and the carbonyl group; attempts to obtain similar derivatives from substances similarly constituted in this respect failed in the cases of 1-phenyl-3-methylpyrazol-5-one, 1-phenyl-5-methylpyrazol-3-one, dimethylaniline, and barbituric acid, but succeeded with malonic acid and its monoalkyl derivatives and with 1-phenyl-2:5-dimethyl-pyrazol-3-one. The following individual substances are described:

antipyrinomethyldimethylamine, $\begin{array}{c}NPh---CO\\NMe\cdot CMe\end{array}{>}C\cdot CH_2\cdot NMe_2$, small

prisms, m. p. 93—94°, which do not yield the colour reactions of antipyrine, and are decomposed into other components by boiling dilute hydrochloric acid (10%) or by sulphurous acid; *hydrochloride*, fine needles, m. p. 208°. *Bisantipyrinomethylmethyl-amine*, $NMe(CH_2 \cdot C_{11}H_{11}ON_2)_2$, needles ($+2H_2O$), m. p. 111°. *Anti-pyrinomethyldiethylamine*, short prisms, m. p. 68°. *Bisantipyrino-methylethylamine*, slender needles, m. p. 143°. *Bisantipyrino-methylallylamine*, shining prisms, m. p. 163° (the base unites with two atoms of bromine in chloroform solution, but the product is not crystalline). *Ethyl bisantipyrinomethyldminoacetate*, needles grouped in rosettes, m. p. 174°. *Bisantipyrinomethyl-ac-tetrahydro-β-naphthylamine*, small, shining leaflets, m. p. 217°. *Antipyrino-methylpiperidine*, plates, m. p. 99°. *Antipyrinomethyltetrahydro-quinoline*, slender needles ($+1H_2O$), m. p. 153°. *Bisantipyrino-methyl-ω-aminoacetophenone*, slender needles, m. p. 93°; *hydro-chloride*, small leaflets, m. p. 96°. *Tetra-antipyrinomethylethylene-diamine*, shining prisms, m. p. 179°. *Bisantipyrinomethylpiper-azine*, m. p. 248° (prisms$+4\cdot5H_2O$). *Antipyrinomethylmethyl-aniline*, small prisms, m. p. 140°. iso*Antipyrinomethyldimethyl-amine*, $\begin{smallmatrix} NPh \cdot CMe \\ | \\ NMe{-}CO \end{smallmatrix}\!\!>\!\!C \cdot CH_2 \cdot NMe_2$, small prisms ($+1H_2O$), m. p. 66°.

Condensation products could not be isolated from antipyrine, formaldehyde, and hydrazine hydrochloride or guanidine hydro-chloride respectively.   H. W.

Preparation of Monoazo-dyes. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 309951; from *Chem. Zentr.*, 1919, ii, 179).— Diazotised 5-nitro-2-aminobenzamides, in which the two hydrogen atoms of the amino-group are replaced by alkyl, aryl, or aralkyl groups, are coupled with the sulphonic acids of β-naphthylamine or its derivatives in acid solution. The products dye wool in red to violet shades from an acid bath, and the dyes are fast to light and rubbing. The nitro-2-aminobenzamides are obtained by the action of secondary aliphatic or aromatic amines on nitroisatoic acid. The following individual members are described: 5-*nitro-2-aminobenz-methylanilide*, m. p. 183—184°; 5-*nitro-2-aminobenzethylanilide*, m. p. 144—145°; 5-*nitro-2-aminobenzdimethylamide*, m. p. 213—214°; 5-*nitro-2-aminobenzpiperidide*, m. p. 163—164°; 5-*nitro-2-aminobenzethyl-o-toluidide*, m. p. 147—148°.   H. W.

Formation of Diazoamino-compounds from β-Naphthyl-amine. GEORGE MARSHALL NORMAN (T., 1919, **115**, 673—679).

Extension of the Theory of Isoelectric Point. Competitive Action of other Ions with H'- and OH'-Ions in the Precipita-tion of Denatured Albumins. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1919, **94**, 225—239).—The coagulation of denatured albumins is dependent on the hydrogen-ion concen-tration. Salts may exert a two-fold action. First, it is shown that other ions than H' and OH' ions may exert an influence on the process. In general, anions displace the optimal hydrogen-ion con-centration for flocculation towards the acid side, whereas cations

exert an opposite effect. The action of the ions is in accordance with the ionic series. Secondly, there may be an inhibition or strengthening of the maximal precipitation at the isoelectric point, as compared with the maximum precipitation in the absence of salts. The earths exert the strongest inhibitory influence, that of the alkalis being less, whilst the heavy metals bring about the reverse effect. Of the anions, chlorine and bromine inhibit, whereas the iodine and CNS ions do not. These actions are a result of a competitive process between other ions and the H˙ and OH′ ions for the protein, which can bind or adsorb them in different amounts. Further knowledge must be based on a systematic investigation of the adsorption of ions by simple adsorbents. J. C. D.

Lysine as a Hydrolytic Product of Hordein. CARL O. JOHNS and A. J. FINKS (*J. Biol. Chem.*, 1919, **38**, 63—66).—Analyses of hordein by the method of Van Slyke indicate that the basic amino-acids are present in the following proportions: cystine 1·18%, arginine 2·82%, histidine 2·27%, and lysine 0·89%. The free amino-nitrogen present in this protein corresponds with one half the lysine nitrogen.

These values agree with those representing the distribution of the basic amino-acids in gliadin from wheat. J. C. D.

Casein. L. A. MAYNARD (*J. physical Chem.*, 1919, **23**, 145—153). —The author has repeated and confirmed the work of Plimmer and Bayliss (A., 1906, i, 325) on the action of 1% sodium hydroxide on casein. It is also shown that the phosphorus of the casein molecule is split off and changed into a soluble inorganic form by the action of 1% sodium hydroxide at 25° for long periods of time. At the same time, the loosely combined sulphur is also split off. On the addition of acids to the sodium hydroxide digest at the end of the digestion, a white precipitate is obtained which, although not identified, has been examined with reference to its dissimilarity from casein. It exhibits colloidal properties similar to those of casein as regards its behaviour with acids and bases. It responds to the various protein tests in the same way as casein, and is similarly precipitated by salts. Its solubility in various reagents is markedly different from that of casein, and a solution in lime-water is quite different from a similar solution of casein. When phosphoric acid was introduced into a lime-water solution, in such a way as not to destroy the colloidal solution, a milky solution was obtained which, on heating, behaved in the same way as a lime-water solution of casein. This reaction furnishes evidence in support of the hypothesis that the white colour of milk is due to the peptisation of calcium phosphate by the colloids in the milk. Attempts to cause this substance to adsorb phosphoric acid were unsuccessful, but the experiments do not necessarily show that such a combination is not present in casein, for both · sulphur and albumoses are also split off by sodium hydroxide, and it may be that their presence is essential for the adsorption of phosphorus.

J. F. S.

Hæmocyanin. I. Reduction of Oxyhæmocyanin by Physical and Biological Means. FILIPPO BOTTAZZI (*J. Physiol. Pathol. gén.*, 1919, **18**, 1—7).—According to Alsberg and Clark (A., 1915, i, 67), oxyhæmocyanin of *Limulus* scarcely gives up any oxygen in a vacuum. The author finds this to be the case for *Octopus* blood, unless it is exposed in thin layers to a very high vacuum, when it is slowly, but completely, decolorised by loss of oxygen. This reduction is also effected by the living leucocytes, even if they are collected as a deposit by centrifuging. If the leucocytes are killed by acids, chloroform, ether, formalin, or are completely removed after centrifuging, the blood remains blue.

G. B.

An Optically Inactive Sodium Nucleate. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1919, **104**, 189—210).—The preparation of a sodium salt of thymus-nucleic acid is described which is optically inactive and will not gelatinise. On the addition of acids, the activity and power of gelatinisation return, and the changes are reversible. The acid groups which hold the sodium in the alkaline salt must be very weak, for the addition of carbon dioxide or acetic acid results in the formation of the active salt. A number of observations are recorded which indicate that the structural changes which underlie the changes in physical properties may occur without corresponding changes in the degree of dissociation of the weak acid groups. It is suggested that these groups are not free in the active molecule, but that they are bound in a form which is sensitive to alkalis, acids, or rise in temperature.

J. C. D.

Adenine Mononucleotide. WALTER JONES and R. P. KENNEDY (*Journ. Pharm. Exp. Ther.*, 1919, **13**, 45—53. Compare this vol., i, 294).—When a neutral or faintly alkaline solution of nucleic acid is oxidised with potassium permanganate, the various groups are destroyed in a definite order, and a residue is obtained from which no cytosine, uracil, or guanine can be isolated after acid hydrolysis. From this residue, an adenine mononucleotide has been isolated crystallising in needles, and giving rise to a crystalline brucine salt, m. p. 173—174°. On the grounds that the nucleotide is a dibasic acid and that it yields adenine on mild acid hydrolysis at a much more rapid rate than it does phosphoric acid, it is concluded that the structure must be

$$PO(OH)_2 \cdot O \cdot C_5H_8O_3 \cdot C_5H_4N_5.$$
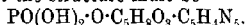
This formula is in accordance with everything that is known of the substance.   J. C. D.

The Effect of Hydrogen Ion Concentration on the Lique-faction of Gelatin. HARRISON E. PATTEN and ALFRED J. JOHNSON (*J. Biol. Chem.*, 1919, **38**, 179—190).—The setting of gelatin is influenced by the hydrogen-ion concentration of the medium, and unless the gelatin is destroyed, this effect is probably reversible.

Gelatin in the concentrations used is not without effect on the buffer solutions, displacing the p_H in such a manner as would be expected from an aggregate of amino-acids acting amphoterically. *

J. C. D.

New Theories of the Formation and Action of Diastase. J. WOHLGEMUTH (*Biochem. Zeitsch.*, 1919, **94**, 213—224).—The author cannot confirm the work of Biedermann (A., 1916, i, 62), who found a diastatic action in boiled starch solution. He is also unable to confirm the experimental results of Woker (A., 1916, i, 61, 447), who claimed that formaldehyde could exert a diastatic action. The severe criticisms of the latter author's work advanced by Kaufmann (A., 1916, i, 62) are supported. A quantitative recovery of starch may be effected after treatment with formaldehyde for twenty-four hours if the aldehyde is removed by phenylhydrazine and alcohol. The starch so recovered gives the typical reactions. The action of the formaldehyde must be, as Kaufmann suggested, due to a combination with the groupings which react with iodine. J. C. D.

Fixation of Formaldehyde by Enzymes. TH. BOKORNY (*Biochem. Zeitsch.*, 1919, **94**, 69—77).—The fixation of formaldehyde by emulsin was studied quantitatively, and from the amount found, assuming that combination of the aldehyde and free amino-groups in the emulsin occurs, it is estimated that 4% of the enzyme is represented by such groups in a reactive state. Previous experiments (A., 1915, i, 1018) gave a lower percentage, but this may be due to differences in the purity of the two preparations. The author interprets these and other results as evidence that emulsin possesses a protein nature. J. C. D.

Biochemical Synthesis of Cellobiose by means of Emulsin. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1919, **168**, 1016—1019).—From the residue left, after extracting gentiobiose and the mono- and di-glucosides of ethylene glycol obtained in the action of emulsin on a mixture of ethylene glycol, dextrose, and aqueous alcohol (see this vol., i, 137), the authors have now isolated and characterised cellobiose. W. G.

Oxidising Enzymes. I. The Nature of the "Peroxide" Naturally Associated with certain Direct Oxidising Systems in Plants. MURIEL WHELDALE ONSLOW (*Biochem. J.*, 1919, **13**, 1—9).—If the tissues of certain plants (pear, potato, apple, and greengage) which give direct oxydase reactions are extracted with alcohol something is removed which is part of the system responsible for the reactions. An aqueous extract of the alcohol insoluble fraction will not darken on exposure to air, nor will it give a blue coloration with guaiacum tincture until hydrogen peroxide is added. If these aqueous extracts, which contain the peroxydase, are treated with catechol or protocatechuic acid, they

darken on exposure and will give the guaiacum reaction. The pear oxydase added to a crude solution of caffeic acid, followed by guaiacum tincture, gave a blue colour. There is reason to believe that the tissues of all plants which turn brown on injury and give the direct reaction with guaiacum will behave in the same manner with catechol and subsequently towards guaiacum. Tissues of plants which normally do not give the direct oxydase reactions failed to yield extracts which oxidised catechol. It is possible that tannin may exert an inhibitory action in some cases. A substance is extracted from pears and potatoes by hot alcohol which is precipitated by lead acetate, is soluble in ether, and gives the reaction with ferric chloride and sodium carbonate characteristic of the orthodihydroxy-grouping of catechol.

The direct oxydases of plants prepared by precipitation of the expressed juices with alcohol have been termed laccases, but it appears probable that these complexes are precipitates containing the crude peroxydase and, in addition, the oxidised aromatic substance in an adsorbed condition. The conception of the oxydase system as formulated by Bach and Chodat is extended. The direct oxydase system in the pear fruit and potato tuber is due to the presence of peroxydase and an aromatic substance, giving reactions characteristic of the catechol grouping. On injury, the peroxydase activates the oxidation of the aromatic substance, with the formation of a peroxide. The peroxide–peroxydase system so formed will then give a blue coloration with guaiacum.

J. C. D.

Physiological Chemistry.

Non-protein Nitrogen of Human Blood. JOH. FEIGL (*Biochem. Zeitsch.*, 1919, **94**, 84—128).—A detailed discussion of the significance of variations in the non-protein nitrogen of the blood, with especial reference to pathological conditions.

J. C. D.

Formation of Glycogen and Sugar at the Expense of Fats. RAPHAEL DUBOIS (*Compt. rend. Soc. Biol.*, 1918, **81**, 689—691; from *Chem. Zentr.*, 1919, i, 113).—The author's experiments, since 1888, with the marmot lead him to the conclusion that sugar and glycogen can be formed directly from fats and indirectly from proteins.

H. W.

The Fat-soluble Accessory Substance. I. Its Nature and Properties. JACK CECIL DRUMMOND (*Biochem. J.*, 1919, **13**, 81—94).—The fat-soluble accessory growth-promoting factor as present in animal fats is not as stable to high temperatures as has

been assumed. The growth stimulating action of the factor present in butter and whale oil may be destroyed by exposure to a temperature of 100° for as short a time as one hour. Lower temperatures may cause destruction, but the process is not so rapid. In the case of whale oil, exposure to 37° for several weeks was found to cause a great deterioration in the amount of the accessory factor present. As far as could be ascertained, this was not due to changes of an oxidative or hydrolytic nature. The vitamine is not extracted from oils by water or dilute acids, but it may be partly removed by extraction with alcohol. Saponification of oils containing the accessory factor, even when conducted at the ordinary temperature and in the absence of water and oxygen, results in disappearance of the growth-stimulating properties. Fat-soluble *A* could not be identified with any known components of fats or with substances frequently associated with fats, such as cholesterol, phosphatides, or pigments. It is suggested that the vitamine may be an ill-defined body resembling an enzyme.　　J. C. D.

The Fat-soluble Accessory Factor. II. Its Rôle in Nutrition and Influence on Fat Metabolism. JACK CECIL DRUMMOND (*Biochem. J.*, 1919, **13**, 95—102).—The fat-soluble vitamine is necessary for maintenance of health in the adult, although for this purpose relatively smaller quantities are required than are necessary for growth and well-being in the young. No obvious pathological lesion has been observed to be a specific result of a deficiency of this accessory factor, but animals so deprived show a very much impaired resistance to bacterial invasion. No direct connexion between the fat-soluble *A* and fat metabolism could be traced. Absorption of fat or fatty acids from the intestinal tract is good, even when the animals are showing a decline in health as a result of the deficiency of this vitamine.
　　J. C. D.

Rôle of the Antiscorbutic Factor in Nutrition. JACK CECIL DRUMMOND (*Biochem. J.*, 1919, **13**, 77—80).—The dietary requirements of the higher animals include, in addition to a satisfactorily balanced ration of proteins, fats, carbohydrates, and mineral salts, an adequate supply of three accessory food factors: (i) fat-soluble *A* ; (ii) water-soluble *B* ; (iii) the antiscorbutic factor, or water-soluble *C*. This confirms the results of Harden and Zilva (this vol., i, 186).　　J. C. D.

Is Lactalbumin a Complete Protein for Growth ? A. D. EMMETT and G. O. LUROS (*J. Biol. Chem.*, 1919, **38**, 147—159).— Lactalbumin is a complete protein in the sense that it is not lacking in any essential nitrogenous cleavage product necessary for growth. Under some conditions, however, diets containing lactalbumin as a sole source of protein do not permit good growth in rats (see also McCollum, A., 1919, i, 186). This is explained by assuming that lactalbumin is either sensitive to certain toxic sub-

stances or that it is a protein unable to adsorb a vitamine other than water-soluble *B*. Lactose added to such unsatisfactory diets has a good effect, which may be due either to its power of overcoming the toxic agent, or to it carrying a water-soluble vitamine other than water-soluble *B*.   J. C. D.

The Retention Power of the Kidney for Dextrose. Can the Calcium in the Perfusion Fluid be Replaced by Strontium, Barium, or Magnesium ? H. J. HAMBURGER and C. L. ALONS (*Biochem. Zeitsch.*, 1919, **94**, 129—130).—The author has previously shown that dextrose may be retained by the frog's kidney perfused with a modified Ringer's solution (Hamburger and Brinkman, *Proc. K. Akad. Wetensch. Amsterdam*, September, 1917). When the perfusion fluid contains 0·06% of dextrose and the calcium is replaced by an equivalent amount of strontium or barium, the sugar is retained by the kidney, but such is not the case when an equivalent amount of magnesium is employed. If the solution is hypertonic with regard to dextrose, 0·1%, the same amount of sugar is found in the urine whether the perfusion fluid contains calcium, barium, or strontium.   J. C. D.

The Formation of Phenol. MIDORI TSUDJI (*J. Biol. Chem.*, 1919, **38**, 13—16).—Phenol, but not cresol, is formed from tyrosine by the action of *Bacillus coli communis*. Phenol was not formed from phenylalanine. The significance of these observations with regard to the formation of phenols in the animal body is considered.
                                                           J. C. D.

Bioluminescence. RAPHAEL DUBOIS (*Compt. rend. Soc. Biol.*, 1918, **81**, 484—485; from *Chem. Zentr.*, 1919, i, 241).—The investigations of Harvey (A., 1917, i, 365; 1918, i, 89) do not justify the replacement of the nomenclature "luciferase" by another name [compare Harvey, this vol., i, 299].   H. W.

The Relationship between Odour and Chemical Constitution. THOMAS H. DURRANS (*Perfumery and Essent. Oil Rec.*, 1919, **10**, 104—136).—The author gives a systematic survey of various classes of chemical compounds containing only carbon, hydrogen, and oxygen, or only two of these elements, and attempts to trace the cause of their odour or the lack of it, certain general conclusions being drawn for each class of compound. It is obvious that certain groups and linkings are sources of odour, but there are undoubtedly other powerful influences at work. Woker's theory that intramolecularly repelling forces increase the volatility of a compound, and consequently its odour, is partly correct, but breaks down with certain classes of ring compounds. A moderate molecular weight increases an odour, but a high molecular weight undoubtedly suppresses it. In certain circumstances, the closing of a ring does not affect the odour much, although in other not very different cases the effect is quite marked.

If the various osmophores, or sources of odour, are examined, it will be noticed that there is always a possibility of unsatisfied partial valencies or residual affinities existing, for example, the oxygen atom, the benzene ring, multiple linking, etc., all sources of odour and all possessing residual affinities.. The author believes that such unsatisfied residual affinities are the prime cause of a chemical substance having an odour. If these affinities can be satisfied intramolecularly, no odour results. Thus the alcohols have unsatisfied residual affinities, the glycols have not; the alcohols have an odour, the glycols have not. It is necessary to assume that these

$$R \cdot \ddot{O}H \qquad \begin{matrix} R \cdot OH \\ | \\ R \cdot OH \end{matrix}$$
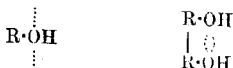
residual affinities can, under certain conditions, neutralise one another, and thus produce no odour, this neutralisation being influenced by the proximity of various groups. Thus with acids we may have

$$\begin{matrix} \cdots O \cdots \\ R \cdot \ddot{C} - OH \\ (I.) \end{matrix} \qquad \text{or} \qquad \begin{matrix} R \cdot C \diagup^{OH}_{O} \\ (II.) \end{matrix}$$
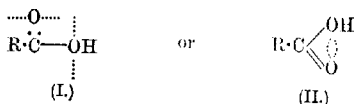
according as R is a light or a heavy group, substance I having an odour and substance II being odourless. On esterifying with an alcohol of low molecular weight, odour is again produced.

W. G.

Oxyhydrase, an Oxidising Reducing Ferment. Its Antitoxic Function. J. E. ABELOUS and J. ALOY (*Compt. rend. Soc. Biol.*; 1918, **81**, 783—785; from *Chem. Zentr.*, 1919, i, 383).—A ferment is present in milk as well as in other vegetable and animal secretions which can reduce nitrates and chlorates in the presence of an oxidisable substance (salicylaldehyde, anisaldehyde). The ferment decomposes water with the liberation of hydrogen and hydroxyl ions, and thus has reducing as well as oxidising power. Oxyhydrase is a factor in the antitoxic defence of the organism, and is adapted to the anærobic life of the cells. H. W.

The Quantitative Excretion of Silicic Acid in Human Urine. M. GONNERMANN (*Biochem. Zeitsch.*, 1919, **94**, 163—173). —Normal human urine contains silica, the excretion of which may be raised by the ingestion of certain mineral waters. J. C. D.

The Treatment of Wounds with the Carrel-Dakin Solution. K. OTTO (*Deut. med. Woch.*, 1917, **43**, 174—175; from *Chem. Zentr.*, 1919, i, 123).—The prescribed method of preparing the solution is too complicated for use in the field, and the following simpler process is recommended. Bleaching powder (200 grams) is

ground with water and addition of the latter is continued with constant stirring until the volume is 7 litres. A solution of sodium carbonate (140 grams) in water (2 litres) is added with stirring, and the solution is filtered. A solution of boric acid (40 grams) in water (1 litre) is added to the filtrate. Since this solution often causes a burning sensation it was later reduced to half strength and, in this form, rendered good service. Treatment with Dakin's solution has chiefly a prophylactic value.   H. W.

Behaviour of Cinnamic Acid and its Derivatives in the Animal Body. HIDEZO ANDO (*J. Biol. Chem.*, 1919, **38**, 7—11).— —α-Benzoylaminocinnamic acid and *o*-benzoylaminocinnamic acid were recovered from the urine unchanged after subcutaneous or oral administration to dogs or rabbits. Only small amounts of α-benzoyl-amino-*p*-hydroxycinnamic acid could be so recovered. Administrations of cinnamoyltyrosine by the mouth were followed by the appearance of hippuric acid in the urine. The substance is apparently broken down by the animal organism.

Cinnamoyltyrosine,
$$OH \cdot C_6H_4 \cdot CH_2 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot CH\vdots CHPh,$$
was obtained as its *ethyl* ester (m. p. 130°) by the action of sodium carbonate on mixed solutions of cinnamoyl chloride and tyrosine ester in chloroform. On hydrolysis with sodium hydroxide, cinnamoyltyrosine was obtained, crystallising in polygonal prisms, m. p. 166—167°.   J. C. D.

Metabolism of the Furan and Hydrofuran Derivatives in the Animal Body. NOBUYOSHI SUZUKI (*J. Biol. Chem.*, 1919, **38**, 1—5).—Hydroxymethylpyromucic acid was isolated from the urine of rabbits which had received subcutaneous or oral administrations of chitose.   J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Absolute and Relative Disinfecting Power of Elements and Chemical Compounds. HANS FRIEDENTHAL (*Biochem. Zeitsch.*, 1919, **94**, 47—68).—An exhaustive study of the disinfecting powers of a large number of products. The relative disinfecting powers of the elements in each group of the periodic classification are given, as well as information regarding many organic disinfectants. [See further, *J. Soc. Chem. Ind.*, 1919, July.]   J. C. D.

The Effects of Acids, Alkalis, and Sugars on the Growth and Formation of Indole by Bacillus coli. FRANK JOHN SADLER WYETH (*Biochem. J.*, 1919, **13**, 10—24).—The activity of

B. coli in 2% peptone is determined by almost the same initial conditions of acid and alkaline reactions as is the case when fermentation is conducted in 2% dextrose peptone. The approximate limits of initial reaction are $p_H = 4\cdot27$ to $9\cdot87$. A change of the initial reaction of the medium results in a change, similar in direction, but smaller in magnitude, in the final reaction of the culture. For *B. coli* grown in 2% dextrose peptone, whilst the initial reactions of the media vary from $p_H = 4\cdot30$ to $9\cdot82$, the final reactions only vary between $p_H = 4\cdot27$ and $4\cdot82$. When grown in 2% peptone the initial reaction may be from $p_H = 4\cdot30$ to $9\cdot37$, and the final reaction from $p_H = 5\cdot92$ to $8\cdot55$.

The proteolytic fermentation resulting in the peptone medium causes an increase of final alkalinity, unless the initial reaction lies between $p_H = 9\cdot37$ and $8\cdot48$, in which case the final reaction is less alkaline than the initial reaction. The saccharolytic fermentation of *B. coli* in 2% dextrose peptone produces approximately constant amounts of acids and no appreciable amount of ammonia; on the other hand, when in a peptone medium the organism produces ammonia and acids in increasing amounts as the initial reaction of the medium increases in alkalinity. Formation of indole is retarded by the presence of free alkali or acid, whilst certain sugars also inhibit the formation of this substance by depressing the proteolytic activity of the bacillus. J. C. D.

The Action of Electrolytes on the Electrical Conductivity of the Bacterial Cell and their Effect on the Rate of Migration of these Cells in an Electric Field. C. SHEARER (*Proc. Cambridge Phil. Soc.*, 1919, **19**, 263—266).—A thick, creamy emulsion of the meningococcus or *B. coli* in neutral Ringer's solution (that is, one in which the sodium hydrogen carbonate is left out) has a resistance, as measured by electrical conductivity determinations, more than treble that of the same solution without the bacteria. If in place of Ringer's solution the emulsions are prepared with a solution of sodium chloride having the same conductivity as the Ringer's solution, a high resistance is obtained at first, but this rapidly drops, and at the end of thirty to forty minutes is the same as that of the saline solution alone. Further, it is found that immersion in such a solution for several hours kills the bacteria. If, when the resistance of such an emulsion in sodium chloride solution has dropped to normal, a little calcium chloride is added, the bacterial emulsion regains its high resistance and the bacteria are uninjured. Potassium, lithium, and magnesium chlorides act like sodium chloride, whilst barium and strontium chlorides act like calcium chloride. These results agree with those obtained by Loeb, Osterhout, and others with animal and plant cells.

The positive tervalent ions of lanthanum nitrate, and cerium and neo-ytterbium chloride and the negative tervalent ions of sodium citrate appear to have no action in increasing or decreasing the resistance of the bacterial cell as determined by the conductivity method, when used in very dilute solutions. On the other hand,

these salts and especially lanthanum nitrate, have a marked action in changing the rate of migration of these bacterial cells in an electric field. The addition of the lanthanum nitrate reduces the rate of migration, or, in other words, considerably alters the nature of the electrical charge on the bacterial cell wall.   W. G.

Decomposition of Betaine by the Bacteria of "Guanol," a Fertiliser Prepared from Molasses Waste. ALFRED KOCH and ALICE OELSNER (*Biochem. Zeitsch.*, 1919, **94**, 139—162).— Organisms were found which attack betaine with the formation of trimethylamine, ammonia, and carbon dioxide. Methyl alcohol, formic acid, and acetic acid in small amounts appear to be the intermediate products in the production of carbon dioxide. [See further, *J. Soc. Chem. Ind.*, July, 1919.]   J. C. D.

Action of Mixtures of Certain Salts on the Lactic Acid Fermentation. CHARLES RICHET and HENRY CARDOT (*Compt. rend. Soc. Biol.*, 1918, **81**, 751—755; from *Chem. Zentr.*, 1919, i, 380).— The action of combinations of antiseptic salts on the lactic acid fermentation has been examined. Action is not additive; the more potent salt (copper sulphate) behaved after addition of cadmium sulphate as if the latter were not present. Addition of the sulphates of copper or zinc did not modify the antiseptic action of cadmium sulphate.   H. W.

Fumaric Acid Fermentation of Sugar. C. WEHMER (*Ber.*, 1919, **52**, [*B*], 562—564).—A reply to Ehrlich (this vol., i, 239) denying that *Rhizopus nigricans* produces fumaric acid. J. C. W.

Influence of Varying Barometric Height on the Course of Alcoholic Fermentation and on Biological Processes in General. AUGUST RIPPEL (*Centr. Bakt. Par.*, 1917, [ii], **47**, 225—229; from *Chem. Zentr.*, 1919, i, 34).—The curves showing loss in weight due to the escape of carbon dioxide during slow fermentation show distinct zig-zags due to variations in the atmospheric pressure, the curve sinking with rising pressure and rising with decreasing pressure. The natural effect of change of pressure on the evolution of carbon dioxide must affect the course of fermentation in proportion as the yeast is influenced by the degree of saturation of carbon dioxide. The same considerations also apply to other biological processes in which a gas is evolved (ammonia, hydrogen sulphide, etc.), and a similar influence must also be operative in nature.   H. W.

Ferment Action. IV. Further Studies on the Adsorption of Mixtures of Amino-acids with Polypeptides and Other Substances. Behaviour of Amino-acids and Polypeptides towards Albumin Solutions, Blood-Serum, and during the Coagulation of Sols. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1918, **2**, 211—224; from *Chem. Zentr.*, 1919, i, 95—96. Compare A., 1917, i, 306; 1919, ii, 49, 50).—The previous

observation that the presence of carbohydrates diminishes the adsorptive power of animal charcoal towards polypeptides, and that conversely the adsorption of carbohydrates is adversely influenced by polypeptides, whilst in the presence of amino-acids the displacement of adsorption is one-sided, is confirmed by further examples. Thus the behaviour of proline is similar to that of other amino-acids, whilst glycine anhydride and pyrrolidonecarboxylic acid behave like dextrose. It is found that amino-acids and polypeptides can, in certain circumstances, be completely displaced by other amino-acids or higher polypeptides without the latter suffering displacement, but that the greater number only cause partial displacement.

The behaviour of various sols in this connexion has also been investigated with the possible aim of measuring the rate of adsorption and investigating its degree of dependence on the hydrogen-ion concentration of the solution. The sols investigated (ferric hydroxide, aluminium hydroxide, and arsenic sulphide) did not, however, adsorb amino-acids and polypeptides during coagulation. On the other hand, glycyl-*l*-leucine was adsorbed by coagulating blood serum. H. W.

Ferment Action. V. Ultrafiltration Experiments with Mixtures of Amino-acids or Polypeptides with Yeast Juice. Evidence for the Colloidal Condition of Ferments and Extension of the Adsorption Theory. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1918, **2**, 225—250; from *Chem. Zentr.*, 1919, i, 96. Compare preceding abstract).—The quantity of water employed in the maceration of yeast has great influence on the activity and stability of the juice. When ten times the amount of water is used, a stable juice, which is immediately active, is obtained; when three times the quantity of water is used, the initial activity of the juice is slight, but increases rapidly on keeping, and finally reaches a maximum which is never attained in the former case. Difference appears to depend on an alteration in the state of the ferment, for example, its dispersivity with dilution. In this connexion, a series of ultra-filtration experiments have been performed. The extracts, obtained from various dried yeasts, had very differing activities towards glycyl-*l*-leucine. Yeast juices mixed with the latter or with *l*-leucine yielded filtrates which were always poorer in amino-nitrogen than the original mixtures, the loss being relatively greater from dilute than from concentrated solution. The originally inactive yeast juices also had power of adsorption, and the equilibrium is independent of the amount of hydroxyl ions present. Adsorption occurs with polypeptides (glycyl-*d*-leucine) which are not attacked by yeast juice. Under equivalent conditions, the adsorption of a complex polypeptide is greater than that of a dipeptide. With decrease in the fermentive activity of a juice by age or by heat a decrease in adsorptive capacity is observed which may sink to zero. Considered in connection with the observation that adsorption can occur with inactive juices, this leads to the deduc-

tion that whilst adsorption of the substrate by the colloidal ferment precedes fission, the latter process does not necessarily follow the former. Further evidence is shown by the behaviour of glycyl-*l*-leucine, which, at 0°, is adsorbed by yeast extract, but not decomposed.

The temperature-coefficient of fission of polypeptides generally lies between 1·3 and 2·4 according to conditions (yeast extract, temperature, hydrogen-ion concentration, and substrate). The optimum temperature for $p_H = 7·50$ is between 50° and 55°.

The chief results of the work in this field are collected and reviewed.   H. W.

The Nitrogenous Constituents of Yeast. JAKOB MEISEN-HEIMER (*Zeitsch. physiol. Chem.*, 1919, **104**, 229—283).—An investigation of the nature of the monoamino-acids present in the products of autolysis derived from bottom and top fermenting yeasts. The estimations were carried out by the ester method of Fischer. Glycine, alanine, valine, leucine, proline, phenylalanine, aspartic and glutamic acids, tyrosine, and tryptophan were identified. Serine and cystine were recognised with less certainty, and there was also evidence of the presence of an aminobutyric acid. Glucosamine was isolated from the cell residue of the autolysis.   J. C. D.

Enzymatic Power of Yeast. TH. BOKORNY (*Allgem. Brau.-Hopf. Zeit.*, 1918, **58**, 1093—1094; from *Chem. Zentr.*, 1919, i, 96—97).—Experiments are described on the inhibiting action of disinfecting agents, even in minute quantity, on the fermentative activity and other enzymatic powers of yeast. Formaldehyde (0·2%) retards growth and fermentation, the yeast is killed, as is also the fermentation ferment; 0·05% does not destroy the activity of the latter. 0·1% kills zymase within two days, but 1% does not render invertase inactive in the same time, sugar solution being strongly inverted. It is therefore possible with the aid of formaldehyde to prepare a yeast which can invert, but not ferment, sugar. Phenyl-hydrazine (0·5%) inhibits the fermentation of maltose, but not of dextrose. Fermentation persists slightly in the presence of mercuric chloride (0·02%), but is inhibited by 0·1%, although sucrose is still powerfully inverted. The action of silver nitrate is similar. Alcohol (10%) does not cause a permanent inactivity of zymase within five days, and, even after twenty days, slight fermentative power persists. Absolute alcohols destroy the power to ferment within ten minutes.
    H. W.

Alterations in the Metabolism and Cellular Permeability at Temperatures near the Freezing Point. E. PANTANELLI (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 205—209).—When cooled to a temperature closely approaching the freezing point, the endo-carp cells of the almond exhibit a progressive increase of the cellular permeability, which is rendered evident by rapid emission of water from the tissue in a dry atmosphere and by exosmosis of substances

from the tissue immersed in water. This phenomenon is accelerated by the presence of certain compounds which penetrate rapidly into the cell, such as glycerol, ethyl alcohol, citric acid, and free alkali. Such increase in cellular permeability is accompanied by rapid destruction of the sugars; this effect may be restricted by supplying either substances capable of being absorbed and utilised for the respiration, for instance, glycerol, ethyl alcohol, or citric acid, or substances which retard the exosmosis of the sugars, or intermediate products of the respiration, such as sodium chloride, potassium phosphate, and citric acid. Sugars (sucrose, dextrose) present in the external liquid do not exert a similar restricting action, since they are not absorbed. A further phenomenon caused by the low temperature is intense auto-digestion of the proteins, this being enhanced by exosmosis of the soluble products of the digestion and by rapid destruction of the sugars.   T. H. P.

Influence of Fluorides on Vegetation. A Preliminary Experiment in Flower Pots. ARMAND GAUTIER and P. CLAUSMANN (*Compt. rend.*, 1919, **168**, 976—982).—As the result of pot trials, using wood charcoal to which the necessary nutrients had been added as a culture medium, the authors find that fluorine in the form of potassium fluoride exerted a favourable influence on the growth of seven species of plants, had no effect on three, and caused a lower crop yield in the case of three.   W. G.

Comparative Rate of Absorption of Various Salts by Plant Tissue [Carrot and Potato]. WALTER STILES and FRANKLIN KIDD (*Proc. Roy. Soc.*, 1919, [*B*], **90**, 487—504).—The rate of absorption of various chlorides, sulphates, nitrates, and potassium salts from solutions of $0.02N$-concentration was measured by the electrical conductivity method. A rapid withdrawal of salt from solution occurred during the first few hours, after which the absorption proceeded to an equilibrium over a period of several days, the curve being approximately logarithmic in the latter case. Cations were absorbed in the orders K, Ca or Na, Li, Mg or Zn, Al, and K, Na, Li, Ca, or Mg, and anions in the orders SO_4, NO_3, Cl, and NO_3, Cl, SO_4, during the initial and equilibrium periods respectively, these results being generally in agreement with those obtained by Ruhland, Fitting, Pantanelli, and Troendle, who failed to differentiate between the initial and equilibrium stages. The rate and extent of intake of one ion of a salt were found to be influenced by the nature of the other ion, and, as previously observed by Rothert and Meurier in the case of aluminium sulphate, aluminium was absorbed much more rapidly than its anion. According to Troendle, the rate of absorption of the metallic ions in any group of the periodic classification increases with the atomic weight. It is pointed out that although this view is not contradicted by the present results, the latter show equally that the initial rate of absorption is largely dependent on the mobility of the ions or diffusibility of the salt, and that the

position of equilibrium appears to be governed by some quite different property, since at this stage the bivalent ions, Ca, Mg, SO_4, are absorbed to a much smaller extent than the univalent ions, K, Na, Cl, NO_3.   W. E. F. P.

Fatty Oil from the Seeds of the Evening Primrose [Oenothera biennis], and a New Linolenic Acid. A.

HEIDUSCHKA and K. LÜFT (*Arch. Pharm.*, 1919, **257**, 33—69).— The air-dried seeds of the evening primrose contain water (13·95%), crude proteins (13·38%), fat (16·93%), fibre (14·56%), nitrogen-free extractives (35·03%), and ash (6·15%). The oil was obtained by extraction of the crushed seeds with ether, and formed a golden-yellow substance resembling poppy oil in taste and odour; it remained completely liquid at 0°, but a few solid particles separated at −11°. It had D^{15} 0·9283, n_D^{40}:1·4722, acid number 0, saponification number 195·2, Reichert-Meissel number 2·61, Polenski number 0·57, iodine number 148·92, Hehner number 94·94, acetyl number 13·9. It was optically inactive and a member of the class of drying oils. The volatile fatty acids consisted mainly of hexoic acid (0·81%). Separation of the unsaturated and saturated fatty acids was effected in the usual manner by means of the lead salts, and the former were brominated in glacial acetic acid-ethereal solution. Under these conditions, a sparingly soluble *hexabromo-γ-linolenic acid*, microscopic needles, m. p. 195—196° (decomp.), separated which, when treated with zinc and alcohol, yielded *γ-linolenic acid* as a yellow substance of unpleasant odour. Tetra-bromo-α-linoleic acid, tetrabromo-β-linoleic acid, and dibromo-oleic acid were identified in the filtrates from hexabromo-γ-linolenic acid. The unsaturated fatty acids contain γ-linolenic acid (2·50%), α-linoleic acid (30·20%), β-linoleic acid (38·11%), and oleic acid (29·19%). Oxidation of the unsaturated fatty acids with permanganate yielded dihydroxystearic acid, a mixture of tetrahydroxystearic acids, and *γ-hexahydroxystearic acid*, minute needles, m. p. 245° (decomp.).

Fractionation of the saturated fatty acids from alcohol or by means of their magnesium salts led to the isolation of palmitic acid and a substance the properties of which agree with those of daturic acid; theoretical considerations caused the authors to doubt the natural occurrence of the latter acid, and experiments on the fractional distillation of the substance with steam showed that the "daturic acid" obtained from the evening primrose, at any rate, was a mixture of palmitic acid (and possibly stearic acid) with acids of greater molecular weight.

The unsaponifiable matter of the oil contained phytosterol (2·27%), the acetate of which had m. p. 130·3° (corr.).   H. W.

Investigations on the Anthocyanin Metabolism on the Basis of the Chemical Properties of the Anthocyanin Group.

K. NOACK (*Zeitsch. Bot.*, 1918, **10**, 561—628; from *Physiol. Abstr.*, 1919, **4**, 99).—A study of *Polygonum compactum* and various

Paeonia species and varieties. In the first days, leaves of *Poly-gonum compactum* have an intense red coloration, which fades away in the following days, and the leaves finally become green. The following explanation of this phenomenon is suggested. Antho-cyanin is dissociated by means of an enzyme into anthocyanidin and sugar. The anthocyanidin is isomerised into a colourless pseudo-base, and this, during its oxidation, can become transformed into a yellow pigment which, by photochemical reduction, may again give the pseudo-base of anthocyanidin. The amounts of antho-cyanidin and its oxidation product vary inversely with one another. The variations are influenced by light, since the pseudo-base is formed by photochemical reduction of the oxidation product of the pigment. In the dark, anthocyanidin is again oxidised, this process being accelerated by heat, light and temperature thus having an antagonistic action. An oxidation product of antho-cyanidin, but not anthocyanidin itself, is found in the vegetative organs of various *Paeonia*, and the amount of this oxidation pro-duct varies directly with the amount of anthocyanin in the plant. In the flowers, in addition to the oxidation product, the antho-cyanidin pseudo-base may occur, but only in small quantities, and without any relation to the amount of anthocyanin formed in the development of the flower.

W. G.

Occurrence of Vanillin. EDMUND O. VON LIPPMANN (*Ber.*, 1919, 52, [*B*], 905).—The occasional presence of vanillin in potato tubers, particularly in the layers immediately beneath the skin, has been frequently observed. It is now found that vanillin can also be extracted from the fresh, blue blossoms (but not from the white ones); it disappears fairly rapidly from the plucked flowers.

H. W.

Preparation of Sucrose from Plants. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, 104, 217—219).—The ether ex-racted fruits of *Sapindus utilis* were extracted with boiling alcohol in the presence of potassium carbonate. The filtered extract, after concentration, was treated with freshly precipitated lead hydroxide for six days. From the lead-free filtrate, a fraction was obtained by extraction with methyl alcohol, which gave sucrose on crystal-isation.

J. C. D.

The Protein Extract of Ragweed Pollen. FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1919, 41, 670—682. Compare A., 917, i, 618).—Three large samples of ragweed pollen have been percolated with ether and 95% alcohol (loss in weight, about 22%). and the residue examined for proteins by repeated macerations with *a*) water, (*b*) 10% salt solution, (*c*) 0·2% potassium hydroxide. The aqueous extract was found to contain an albumin (1·2%), coagulating at about 45—50°, and proteoses (3%), and when partly saturated with ammonium sulphate gave a precipitate consisting of albumin and proteose in the proportion 3:1, and causing

anaphylaxis in guinea-pigs.   After precipitating all the protein from this extract by means of ammonium sulphate, and then removing the sulphate, phosphotungstic acid gave a precipitate of the following bases: adenine, guanosine (?), histidine, arginine, lysine, and agmantine, these being identified by the usual methods. The 10% salt extract gave a small amount of the above albumin and but very little evidence of the presence of a globulin. The dilute alkali extract contained the chief protein, which is therefore a glutelin, amounting to about 2·9% of the weight of the pollen, and appearing as an almost white, dusty powder.   J. C. W.

A Proximate Analysis of Rumex crispus, and a Comparison of its Hydroxymethylanthraquinones with those from Certain Other Drugs. GEORGE D. BEAL and RUTH E. OKEY (*J. Amer. Chem. Soc.*, 1919, **41**, 693—706).—An examination of the extract made by percolating the dried and powdered root of the common yellow (curled) dock with cold 95% alcohol. The constituents which are soluble in water, yielded small quantities of emodin, a mixture of emodin monomethyl ether and chrysophanic acid, dextrose and a little lævulose, and organic acids and much resinous material. The insoluble portion of the extract contained emodin, its monomethyl·ether, chrysophanic acid, a phytosterol, palmitic, stearic, and erucic acids with lower unsaturated and higher saturated fatty acids, a small amount of a hydrocarbon, an essential oil, some glucosides, and much resin.

A cursory examination of cascara and aloes has also been made, mainly with the aim of isolating their emodins. *Rumex* emodin is identical with that of cascara (Jowett, A., 1905, ii, 192) and isomeric with the aloe-emodin of aloes and senna. The phytosterol is also the same as the "rhamnol" of cascara.

The yield of emodin from the dried dock root is about 0·1%, and that of chrysophanic acid somewhat less. This compares favourably with the quantities obtainable from more expensive drugs.
                                                                        J. C. W.

Toxicity of "Alkali" Salts. THAKUR MAHADEO SINGH (*Soil Sci.*, 1918, **6**, 463—477).—An examination of the effect of various sodium salts on ammonifying, nitrifying, and nitrogen-fixing organisms, and on the germination and growth of wheat and peas. Arranged in order of descending toxicity, the salts examined are sodium chloride, nitrate, carbonate, and sulphate, the percentage of the anion, and not of the cation, being the determining factor. Small amounts of each of the different salts used stimulated both crop growth and bacterial activity, the amount varying with the crop grown. The toxicity point as found when salts were used in combination, as under field conditions, agreed very closely with the points found when the individual salts were used. The toxic point of the combined salts depended on the percentages of the chlorides, nitrates, carbonates, and sulphates present, and the combination in which they existed. Calcium sulphate when present

lowered the toxic point of the chloride, carbonate, or nitrate of sodium. W. G.

Alfalfa [Lucerne] Investigation. VII. Alfalfa Saponin. C. A. JACOBSEN (*J. Amer. Chem. Soc.*, 1919, **41**, 640—648).—When alfalfa hay is extracted with hot alcohol and the solution is cooled, a voluminous, green precipitate is deposited, from which ether extracts two ketones, myristone and alfalfone (A., 1912, ii, 80; i, 239). The insoluble, gummy residue left in the Soxhlet thimble contains a saponin, which may be isolated by dialysis of the aqueous solution and reprecipitation with alcohol. Alfalfa [lucerne] *saponin*, $C_{27}H_{37}O_{16}N$, is a brown, amorphous powder, decomp. 280—300°, readily soluble only in water and glycerol, and may be hydrolysed to a *sapogenin*, $C_{18}H_{18}O_{10}N$, dextrose, and a pentose. It also forms an *acetyl* derivative, but this may be the acetate of the sapogenin. Its solution has an enormous surface tension, minute quantities producing a remarkable foam in aerated beverages, and bubbles 4 inches in diameter being possible with a 25% solution.

The saponin differs from most compounds of this type in containing nitrogen. It is also abnormal in that it does not hæmolyse blood. It is toxic to fish, but this generally accepted property of saponins as a class seems to be due to their power of preventing the diffusion of air into the water, for the golden carp, which has the instinct to rise to the surface to breathe, will live in saponin solutions (1 to 35,000), whereas the black bass succumbs. Alfalfa saponin causes acute local irritation and death when injected subcutaneously, but is harmless when taken *per os*.

The crude saponin is accompanied by a yellow substance, "saponin X," and alfalfa also contains two proteins and a bitter principle, which are being investigated. J. C. W.

Effect of Manganese on the Growth of Wheat. A Source of Manganese for Agricultural Purposes. J. S. McHARGUE (*J. Ind. Eng. Chem.*, 1919, **11**, 332—335).—Results of pot cultures showed that the addition of manganese increases the size and nitrogen content of wheat grains, and stimulates the growth of the plant; the most favourable quantity appeared to be about 0·028% of manganese, calculated on the total weight of the soil in the pot. It was added in the form of manganese carbonate. Basic slag contains an average of 4·8% of manganese, and it is possible that some of the benefit to crops resulting from the use of this fertiliser is due to the presence of manganese. W. P. S.

Solubility of the Calcium, Magnesium, and Potassium in such Minerals as Epidote, Chrysolite, and Muscovite, especially in regard to Soil Relationships. R. F. GARDINER (*J. Agric. Res.*, 1919, **16**, 259—261).—When the finely powdered minerals were left in contact with the aqueous extract from an acid soil for two months at 25°, it was found that 1·6% of the total calcium in the epidote, 0·21% of the magnesium in the

chrysolite, and from 11 to 21% of the potassium in the muscovite was extracted under the experimental conditions.   W. G.

Decomposition of Cyanamide and Dicyanodiamide in the Soil. G. A. COWIE (*J. Agric. Sci.*, 1919, **9**, 113—136).—Experiments on field plots and on soil in pots show cyanamide to be decomposed in soil, yielding ammonia, which is then nitrified in the usual way. The conversion of the nitrogen of the cyanamide into nitrate is almost quantitative. Dicyanodiamide undergoes no decomposition. On adding both substances together to soil, it is found that the dicyanodiamide does not prevent the formation of ammonia from the cyanamide, but that it largely prevents nitrification. In a mixture of the two substances containing 25% of dicyanodiamide, only 22% of the nitrogen is converted into nitrate, and in a mixture containing 75% of dicyanodiamide, only 5%. Dicyanodiamide is thus toxic to the nitrifying organisms. On the ammonifying bacteria it has no effect, as dried blood readily undergoes ammonification in its presence, and the ammonia produced accumulates in the soil owing to the action of the nitrifying organisms being prevented. These results show that cyanamide is not normally converted into dicyanodiamide in soil; they also suggest the possibility of a di-imino-formula for dicyanodiamide. [See also *J. Soc. Chem. Ind.*, 1919, 380A.]   J. H. J.

Soluble Non-protein Nitrogen of Soil. R. S. SNYDER and R. S. POTTER (*Soil Sci.*, 1918, **6**, 441—448).—From a further study of the method previously described (A., 1917, i, 75), the authors find that, in order to obtain the maximum soluble non-protein nitrogen from basic soils, they should be extracted with 1% hydrochloric acid until the washings show no calcium. It is unnecessary to extract acid soils with the acid. Nitrates in the acid extract may be reduced by Devarda's alloy after making the extract faintly alkaline. The examination of a number of soils shows that the amount of the unknown soluble non-protein nitrogen is usually decreased by an application of lime, although there are exceptions.
W. G.

Manuring Experiments with "Kalikalk." H. G. SÖDERBAUM (*Medd.* No. 163, *Centralaustalten försöks. jordbruk;* from *Bied. Zentr.*, 1919, **48**, 135—136).—This preparation (prepared by heating together potash felspar, limestone, and gypsum at 1150°) gave good results in the manuring of oat crops. [See further, *J. Soc. Chem. Ind.*, 1919, July.]   J. C. D.

Organic Nutrients for Green Plants. TH. BOKORNY (*Biochem. Zeitsch.*, 1919, **94**, 78—83).—Sulphite lye from the cellulose industries, even after the removal of the majority of the sugar, is of considerable value as a manure. The value of human urine as a nutrient for plants is also great. The presence of hippuric acid in the urine of certain domestic animals makes this waste product less useful than human urine. This may be due to the toxic influence of the benzoic acid.   J. C. D.

General and Physical Chemistry.

Ultra-violet Band of Ammonia and its Occurrence in the Solar Spectrum. A. FOWLER and C. C. L. GREGORY (*Phil. Trans.*, 1919, [*A*], **218**, 351—372. Compare A., 1918, ii, 282).—The ammonia spectrum has been photographed (i) by means of a quartz spectrograph giving a dispersion of 60 Å. per mm. at λ 3360, (ii) by a quartz Littrow instrument having a dispersion of 7 Å. per mm., and (iii) by means of a 10 ft. grating giving a dispersion of 1·85 Å. per mm. In the first two cases an ammonia flame was used, obtained by feeding a blowpipe with ammonia and oxygen, whilst in the last case a copper arc burning in ammonia furnished the light. Long tables of wave-lengths are given, which are probably accurate to 0·01 Å.; these are compared with the Rowland values for the solar spectrum. From the comparison, it is evident that the band λ=3360 in the solar spectrum is due to ammonia, and also that many of the unidentified weaker lines of the solar spectrum are also due to ammonia. Photographs of the highly resolved band λ3360 are appended to the paper. J. F. S.

Wave-length Measurement in Spectra from 5600 Å. to 9600 Å. W. F. MEGGERS (*Bull. Bureau of Standards* [*U.S.A.*], 1918, **14**, [3], 371—395).—The first-order spectra of lithium, sodium, potassium, rubidium, cæsium, copper, glucinum, calcium, strontium, barium, and magnesium have been photographed over the long wave regions 5600 Å. to 9600 Å. For this purpose, a concave grating of radius of curvature 640 cm. with a ruled surface 7·5 cm. by 13·3 cm. with 299 lines per mm. was employed, and was mounted in parallel light, the intensity of the spectra, compared with that afforded by the Rowland method of mounting, being quadrupled by this method of mounting. The device also secures freedom from astigmatism. Ordinary photographic plates were sensitised to the long wave region by being soaked for three to five minutes in a bath made by adding 4 c.c. of a solution of 1 part of dicyanin in 1000 parts of alcohol to 50 c.c. of distilled water, 50 c.c. of ethyl alcohol, and 5 c.c. of strong ammonia. The exposures were limited to thirty minutes. Arcs of metallic electrodes were employed wherever possible, Acheson graphite electrodes impregnated with large quantities of the respective salts being employed in other cases. A current of 6 amperes was employed for the region 6000 Å. to 7000 Å., 7 amperes for the region 7000 Å. to 8000 Å., and so on, except in the case of magnesium, a current of 3 amperes at 110 volts being employed in this case. The comparison spectra were afforded by that of an arc between Norwegian iron poles operated under standard conditions. The results obtained are expressed in tabular form, which afford ready comparison with the results of other observers. The intensities and other physical characteristics of the various lines are recorded. Illustrations of the spectra are

given in some cases. The probable error is less than 0·02 Å. for all lines measured more than twice. The frequency differences of doublets in the spectra of sodium, potassium, rubidium, cæsium, and copper are shown to be constant in most cases to 1 part in 100,000 in the number of waves per cm.   J. S. G. T.

The Serial Constitution of Absorption Spectra. FRED. VLÈS (*Compt. rend.*, 1919, **168**, 1044—1047).—A continuation of previous work (compare A., 1914, ii, 400) in which the author, from a study of the absorption spectra of several substances, confirms his views as to the serial constitution of these spectra.
W. G.

Absorption and Constitution of the Coloured Alkali Salts of Nitrotriphenylmethanes and Related Compounds. A. HANTZSCH and F. HEIN (*Ber.*, 1919, **52**, [*B*], 493—509. Compare A., 1907, i, 500; and Hedley, 1908, i, 382).—A comparison of the alkali salts of nitrotriphenylmethanes and nitrodiphenylamines, nitrohydrazobenzenes, and nitrodiazoaminobenzenes.

Triphenylmethane only forms a mono- and a tri-nitro-derivative. Diphenyl-*p*-tolylmethane (from benzhydrol and toluene by means of stannic chloride) reacts with fuming nitric acid to give 4 : 4'-*dinitro-diphenyl*-o-*nitro*-p-*tolylmethane*, m. p. 131°.   *p*-Bromotriphenyl-methane, however, gives 4-*bromo*-4' : 4''-*dinitrotriphenylmethane*, white leaflets, m. p. 165·5°. The salts of nitrotriphenylmethanes are much less stable than those of the simple nitromethanes, and can scarcely be isolated. Solutions of the mononitro-compounds in alcohol remain colourless for a moment on the addition of sodium ethoxide, but reach the maximum yellow colour in about fifteen minutes. The absorption bands are similar to those of the mono-nitromethane *aci*-salts, but include a quinonoid band, showing that the salts have the simple quinonoid, as well as the *aci*-configuration, thus : $CHPh_2 \cdot C_6H_4 \cdot NO_2 + EtONa \longrightarrow CPh_2 \cdot C_6H_4 \cdot NO \cdot ONa$. The dinitro- and trinitro-compounds give violet salts, which have the " conjugated–quinonoid " configuration of the di- and tri-nitro-methanes, thus :

$$C_6H_4Br \cdot C {\displaystyle\mathop{<}^{C_6H_4 \cdot NO_2}_{C_6H_4 \cdot NO_2}} Na \quad \text{and} \quad NO_2 \cdot C_6H_4 \cdot C {\displaystyle\mathop{<}^{C_6H_4 \cdot NO_2}_{C_6H_4 \cdot NO_2}} Na.$$
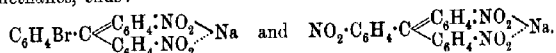
They also give violet salts with ammonia and aliphatic amines, but not with pyridine.

[With M. HARDTMANN].—*p*-Nitrodiphenylamine is best obtained by nitrating pure benzoyldiphenylamine and then hydrolysing by means of alcoholic potassium hydroxide. Its solution in alcohol is pale yellow, but becomes deep red on the addition of potassium hydroxide, owing to the formation of a para-quinonoid salt of the formula $NPh \cdot C_6H_4 \cdot NO_2K$. The *o*-nitrodiphenylamine is yellowish-red in alcoholic solutions, but the addition of potassium hydroxide has no effect. *p* : *p'*-Dinitrodiphenylamine, like the di-, tri-, and hexa-nitrotriphenylmethanes, gives deep violet salts. Strange to say, the salts of hexanitrodiphenylamine are only yellowish-red.

p-Nitrodiazoaminobenzene, *pp'*-dinitrohydrazobenzene, and *pp'*-dinitrodiazoaminobenzene also give violet salts. The last compound is obtained by the action of amyl nitrite on *p*-nitroaniline, but a drop of acetic acid is essential to the initiation of the reaction. Its *sodium* salt, $C_{12}H_8O_4N_5Na$, separates on cooling a solution in aqueous-alcoholic sodium hydroxide, in leaflets with metallic lustre and red streak, which are hydrolysed by cold water to the free aci-*dinitro-diazoaminobenzene*, $NO_2 \cdot C_6H_4 \cdot N:N \cdot N:C_6H_4:NO \cdot OH$. This looks so much like the salt that it has previously been unrecognised. It is even formed when dilute solutions of the ordinary dinitro-compound are boiled and quickly cooled, but it is immediately isomerised by alcohol. When slowly heated, it changes into the more stable form and then explodes at about 233°.

Absorption curves are reproduced in the original and discussed at some length partly in a controversial manner.   J. C. W.

Absorption and constitution of the Simplest Triphenylmethane- and Azo-Dyes and Related Compounds. A. HANTZSCH (*Ber.*, 1919, **52**, [*B*], 509—530).—The absorption bands of the simplest and most important dyes, namely, those of the triphenylmethane series and the azo-dyes, are compared with those of closely-related coloured substances, including the salts of the polynitrotriphenylmethanes (preceding abstract). It is shown that the original quinonoid formulæ given by E. and O. Fischer need only to be extended to conjugated-quinonoid structures to explain the optical properties, new schemes like those of Baker (T., 1907, **91**, 1490) being unnecessary.

In the case of the quinonoid salts of aminotriphenylmethanes, as in the case of the quinonoid alkali salts of nitrotriphenylmethanes, the maximum optical effect, that is, the typical colour, is already reached when there are two salt-forming groups in the molecule. A third amino-group actually has, if anything, a hypsochromic effect. A hydroxyl or methoxyl group in the place of a third amino-group has about half the optical effect; for example, hydroxy- and methoxy-malachite-greens are midway between malachite-green and crystal violet. Tetramethyldiaminorosaniline gives solutions of many colours, from bluish-red to yellow, in indifferent media, but they all give absorption curves like that of magenta, only more or less displaced.

The magenta dyes also closely resemble the reddish-violet salts of the aminoazobenzenes, and the three classes are, therefore, characterised by two components: (1) a quinonoid salt complex (*aci*nitro-salt or ammonium salt) as chromophore, and (2) another group (nitro- or amino-) which forms a powerful auxochrome in conjugation with the quinonoid group, thus:

$$\underset{\text{Nitrotriphenylmethanes.}}{\overset{\displaystyle ArC{=}C_6H_4{=}NO_2}{\underset{\displaystyle Ar \cdot NO_2 \dots M}{|\qquad\qquad|}}} \quad \underset{\text{Aminotriphenylmethanes.}}{\overset{\displaystyle ArC{=}C_6H_4{==}NR_2}{\underset{\displaystyle Ar \cdot NR_2 \dots X}{|\qquad\qquad|}}} \quad \underset{\text{Aminoazo-salts.}}{\overset{\displaystyle N{=}C_6H_4{==}NR_2}{\underset{\displaystyle NAr \cdot R \dots X}{|\qquad\qquad|}}}$$
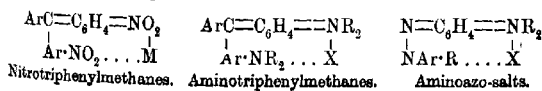
The effect of an acid on compounds of the last types is obviously to break the conjugation and so destroy the auxochrome.

Two new compounds are described. *Dimethoxydimethylamino-triphenylcarbinol*, $(OMe \cdot C_6H_4)_2C(OH) \cdot C_6H_4 \cdot NMe_2$, bundles of very pale green crystals, m. p. 112°, is obtained by heating together dianisyl ketone, dimethylaniline, and a mixture of phosphorus penta- and oxy-chlorides, and is converted into *dimethoxyfuchsondimethyl-imonium chloride*, $(OMe \cdot C_6H_4)_2C:C_6H_4:NMe_2Cl$, by means of hydrochloric acid. This dye has the typical appearance of cantharides, but it is not fast to light or washing.

Several sets of curves are reproduced in the original, but the lengthy discussion is largely polemical.   J. C. W.

Relationship between Mechanical and Chemical Rotation and the Structure of Liquid Crystals. O. LEHMANN (*Ann. Physik*, 1919, [iv], **58**, 631—656).—A continuation of previously published work (*ibid.*, 1916, **51**, 353). The effects produced when the containing walls which hold liquid crystals are twisted whilst polarised light is passing through the crystals are investigated. The effects are examined by means of crossed nicols for *p*-azoxyphenetole and for the same substance to which colophony and cholesteryl benzoate have been added. Numerous diagrams of the appearance under the nicols are given.   J. F. S.

The Rotation Dispersion of Butyl, Heptyl, and Octyl Tartrates. PERCY FARADAY FRANKLAND and FREDERIC HORACE GARNER (T., 1919, **115**, 636—661).

Evolution of Very Dilute Solutions of Tetrachloroplatinic Acid in Complete Darkness and at Different Temperatures. MARCEL BOLL (*Compt. rend.*, 1919, **168**, 1108—1111).—A comparison of the changes and their velocities taking place in a very dilute solution of tetrachloroplatinic acid in the dark at temperatures between 10° and 100°, and those taking place in the light (compare A., 1912, ii, 407). The thermal acceleration is practically the same whether the action takes place in the dark or under the influence of high-frequency rays.   W. G.

Collision of α-Particles with Light Atoms. I. Hydrogen. SIR E. RUTHERFORD (*Phil. Mag.*, 1919, [vi], **37**, 537—561. Compare E. Marsden, A., 1914, ii, 407; Marsden and Lantsberry, *Phil. Mag.*, 1915, [vi], **30**, 240).—"H"-particles, derived by passing α-particles through hydrogen, from "head-on" collisions between the α-particles and the nuclei of the hydrogen atoms, are also obtained, without using hydrogen, from thin-walled glass and quartz tubes filled with radium emanation, and from a deposit of radium-*C* on a nickel plate—from the latter more than the former. Special experiments showed that radium-*C* is not different in this respect from radium-*A* and the emanation, and these have also shown that oxygen and nitrogen atoms (see succeeding papers) can be put in

swift motion by collision with α-particles to cause scintillations outside the range of the α-particles, to which, probably, a large number of the scintillations, ascribed by Marsden to H-particles, were due. The homogeneous α-rays of radium-C deposited on a metal disk were exclusively used. The disk was washed with alcohol and heated in an exhausted tube to 300° for a minute to reduce "volatilisation" of the radium-C (Ratner). The H-particles were counted by the scintillations on zinc sulphide screens, and were similar to those produced by α-particles 3 mm. from the end of their range. The active disk was mounted in a tube capable of exhaustion, or of being filled with the gas studied, at a variable distance from an opening in the end covered with thin sheets of silver, aluminium, or iron of stopping power equivalent to from 4 to 6 cm. of air, the zinc sulphide screen being just outside the apparatus. The number of H-particles is ordinarily less than one in one hundred thousand of the α-particles, and can only be detected after the latter have been absorbed. β-Rays were suppressed by a strong magnetic field. The number of H-particles without any gas in the vessel was first determined. These are small in number relatively to those produced when the apparatus is filled with hydrogen, and it cannot be decided whether they originate from the radio-element itself or from hydrogen occluded by the materials in which it is contained. The number fell off, when metal screens were interposed, rapidly between the equivalent of 7 and 12 cm. of air, and then more slowly, a few being observed up to the equivalent of 28 cm. The metal screens—silver and aluminium—were heated to drive off occluded gases. Gold was found to be very free from hydrogen, but could not be used close to the zinc sulphide screen on account of the marked luminosity it produces on the screen beyond the range of α-particles, an effect that is being investigated.

The number of H-particles produced in hydrogen gas and their distribution with velocity differed markedly from the results calculated from the simple theory by Darwin's formula. The apparatus being filled with hydrogen at atmospheric pressure, the number of H-atoms was counted when aluminium foils were interposed before the screen. There was no diminution between the equivalent of 9 and 19 cm. air absorption, and then a slow decrease in the number took place, followed by a rapid one near the end of the range. Theoretically, between 9 and 19 cm. the number should have been reduced to 28%. This is only marked when long-range α-particles are used. As the range of the α-particles is reduced, the theoretical curves are more and more nearly approached. The absorption curve for H-particles produced by long-range α-particles is similar to that of the α-particles themselves, showing that the hydrogen atoms are thrown forward all at practically the same velocity and in the same direction as the α-particle is travelling, or at least within 10° or 15° from it. The fraction of the number of α-particles which produce one H-particle per cm. of path in hydrogen at $N.T.P.$ was found to be about 10^{-5}. At 10 cm.

(eq. air absorption), the total number produced is ten times, at 19 cm. thirty-one times, the number calculated from the simple theory (Darwin). On the average, each α-particle of 7 cm. range of radium-C produces an H-particle when the perpendicular distance of its path from the centre of the hydrogen atom is equal to or less than $2 \cdot 4 \times 10^{-13}$ cm., and the results point to the view that within $3 \cdot 5 \times 10^{-13}$ cm., the field of force between the colliding nuclei undergoes rapid changes in magnitude, and probably direction. Since only one in 10^5 α-particles passing through 1 cm. of hydrogen produces an H-particle, and in this distance each α-particle passes through 10^4 hydrogen molecules, only one out of every 10^9 collisions produces an H-particle capable of being detected beyond the range of the α-rays. The helium nucleus, or α-particle, is pictured as a charged disk of radius about $3 \cdot 6 \times 10^{-13}$ cm., with its plane perpendicular to its direction of motion, and probably composed of four hydrogen nuclei and two nuclear electrons. This is regarded as being probably much deformed during close collisions. It is to be expected that it would break up, but no evidence of this has yet been observed.   F. S.

Collision of α-Particles with Light Atoms. II. Velocity of the Hydrogen Atom. Sir E. RUTHERFORD (*Phil. Mag.*, 1919, [vi], **37**, 562—571).—The assumption in the preceding paper that the long-range scintillations observed in hydrogen are due to hydrogen atoms set in swift motion by their collision with α-particles is supported by their range, which agrees with that calculated for such H-particles by Darwin from Bohr's theory. The mass, charge, and velocity of these H-particles have been determined by measurements of the deflection they undergo in electromagnetic and electrostatic fields. As source of hydrogen, a film of paraffin wax 30μ in thickness exposed to intense α-rays was used. The H-particles were passed through two slits and received on an external zinc sulphide screen, after passing through a sheet of iron, closing the end of the apparatus, equivalent in stopping power to 4 cm. of air. With the apparatus exhausted, the deviation in a magnetic field of the α-particles themselves was first found. The paraffin film and aluminium screens, equal in total stopping power, with the iron sheet, to 14·4 cm. of air, were then interposed, and the deflection of the H-particles found to be 1·45 times that of the α-particles of radium-C. This gives for mu_0/e, the product of the mass and initial velocity of the fastest H-particles divided by the charge, $3 \cdot 15 \times 10^5$. From theory, u_0 should be $1 \cdot 6$ v_0, that is, $1 \cdot 6$ times that of the α-particles, and mu_0/e $3 \cdot 2 \times 10^5$. All the H-particles carried a positive charge, and no sign of negatively charged particles was observed. The electrostatic deviation between two parallel plates 6 cm. long and 1·55 mm. apart charged to 4500 volts was insufficient to deviate the H-particles completely, and it was calculated that 30,000 volts would be required. So the deflexion with a magnetic field was compared with that produced by a combined electrostatic and electromagnetic field acting in unison, and it was

found that a magnetic field of 238 gauss on the average was equivalent to an electric field of 1000 volts. This gives for u_0 the maximum velocity of the H-particle, 3.12×10^9 cm. per second. The calculated value, $1.6\ v_0$, is 3.07×10^9 cm. per second. The value of e/m, consequently, is 10^4 e. m. units, which agrees very well with the value, 9570, for the H-ion in the electrolysis of water. This proves that for close collisions the conservation of momentum and energy holds good, and that there is no sensible loss of energy due to radiation.

The energy communicated to the H-particle is 0·64 that of the α-particle, and, after traversing the equivalent of 12 cm. of air, is 0·44, corresponding with that of an α-particle of range 2 cm. of air. The brightness of the scintillation it produces is, at all ranges, much less than is to be expected, and corresponds, for example, with that of an α-particle of range 0·5 cm. instead of 2 cm. This may be due to the energy spent per unit of path by an H-particle being only about one-sixth of that by an α-particle. A large proportion of instantaneous double scintillations was observed, and it was found, in comparison with α-particles, that the number was nearly double what is to be expected from probability considerations. It could not be settled, however, whether this effect is real or due to the eye being unable to distinguish separately the weak scintillations due to H-particles as readily as those produced by α-particles.   F. S.

Collisions of α-Particles with Light Atoms. III. Nitrogen and Oxygen Atoms.

Sir E. RUTHERFORD (*Phil. Mag.*, 1919, [vi], 37, 571—580).—From Bohr's general theory of the absorption of charged atoms in passage through matter, which is substantiated experimentally for the α-particles and H-particles, the range x in hydrogen of an atom of charge e and mass m moving with a speed equal to that of an α-particle of range R is given by $x/R = mE^2/Me^2$, M and E being the mass and charge of the α-particle. For light atoms, with unit charge $x = mR$. Tables are given for x/R for singly charged atoms from hydrogen to gold travelling with a velocity calculated to be produced by impact of the atom in a "head-on" collision with the α-particle. For α-particles of range 7 cm., the maximum ranges in cm. to be expected are as follow: He 28, Li 19·6, Gl 15·4, B 12·4, C 11·2, N 9·3, O 7·8. Experiments with helium have shown that, if any long-range particles are produced, the number is very small compared with that produced in hydrogen, and it is concluded that the helium atoms carry a double charge and have the same range as the α-particles. Neither were any certain indications of long-range particles obtained for salts of lithium, glucinum, and boron. Such experiments are much easier for gases, and in air numerous bright scintillations are observed for distances 2 cm. beyond the range of the α-particles. With a total absorption equivalent to 7·5 cm. of air, these "N-particles" and "O-particles" give scintillations equal in brightness to an α-particle of range about 1 cm. The scintilla-

tions for oxygen and carbon dioxide were of about the same range and brightness as those in air, but they were shown to arise in the gases, and not to be emitted from the radio-element itself. No evidence of singly charged carbon atoms from carbon dioxide was obtained. Estimating the relative numbers of high-speed particles in hydrogen, oxygen, and nitrogen, it was found that the numbers for the different gases are not very different. The long-range rays of range 11·3 cm. found by Rutherford and Wood in the active deposit of thorium (A., 1916, ii, 282) are such as would result from oxygen atoms present in the mica screens used, but the number— 1 to 10,000 α-particles—was much greater than is to be expected from the experiments with radium-C, and further experiments are in progress.   F. S.

Collisions of α-Particles with Light Atoms. IV. An Anomalous Effect in Nitrogen. Sir E. RUTHERFORD (*Phil. Mag.*, 1919, [vi], **37**, 581—587).—A surprising effect was noticed in the study of the "natural" scintillations due to H-particles, which it is difficult to decide whether they are due to the action of α-particles on occluded hydrogen in the radioactive material or support, or are expelled in the disintegration itself. With the apparatus described in the first paper, exhausted and filled with dry oxygen or carbon dioxide respectively, the number of natural scintillations observed diminished in about the ratio to be expected from the stopping power of the gas column. In dried air, however, the number increased, and with a total absorption equivalent to about 19 cm. of air was twice as great as with the apparatus exhausted. All experiments were made at absorptions greater than the equivalent of 9 cm. of air to eliminate the O-particles and N-particles described in the last paper. The additional H-particles were not due to moisture or dust nuclei, and were observed in chemically prepared nitrogen, from ammonium nitrate, to an extent 1·25 times that observed for air. They were shown to arise from the volume of the gas, and were not due to a surface effect in the radioactive source. The H-particles so obtained from nitrogen had a somewhat greater penetrating power than those from hydrogen, but none could be detected beyond a range of 28 cm., and probably the difference is due to their being projected more in the line of flight of the α-particles than those resulting from hydrogen gas. The number from nitrogen at atmospheric pressure is equal to the number given in hydrogen at 6 cm. pressure, so that only one H-particle is given in nitrogen for every twelve collisions giving rise to N-particles. As regards both the brightness of the scintillations and the range, these long-range particles closely resemble, and in all probability are, H-particles, but to settle the point definitely it will be necessary to determine their deflexion in a magnetic field. Preliminary experiments indicate a similar deflexion, but to decide the question definitely it will probably be

necessary to employ a solid nitrogen compound free from hydrogen, and to discriminate between H-particles and possible particles of atomic mass 2.

If they are H-particles, it must be concluded that the nitrogen atom has been disintegrated during the close collision with an α-particle, and that the hydrogen nucleus is a constituent part of the nitrogen nucleus. This may account for the ranges of the N-particle and O-particle being the same, instead of differing by some 19%, as is to be expected. For if hydrogen is disrupted from the nitrogen atom, the energy of the impact would be shared between the two systems. Nitrogen is the only light atom of atomic mass $4n + 2$, where n is a whole number, and its nucleus should consist of three helium nuclei and ten hydrogen nuclei. The latter may be outsiders of the main system of mass 12, and the close collision with an α-particle seems to be the most likely agency to promote the disruption of such a nucleus. It is not to be expected, a priori, that the velocity or range of H-particles, so produced from the nitrogen atom, should be identical with that of those produced by collisions in free hydrogen.   F. S.

Precision-measurements in the X-ray Spectra. MANNE SIEGBAHN (*Phil. Mag.*, 1919, [vi], **37**, 601—612).—By a new method of measurement, the accuracy of wave-length measurements for X-rays has been increased a hundred-fold. The angle of the reflected rays is determined as the angle through which the same photographic plate has to be turned in order to receive impressions of the nth order reflection on both sides of the direct ray, the angles being read off an accurate circle scale. If ϕ is the angle of reflexion, and the plate is turned accurately 4ϕ (and the crystal nearly $2\phi + 180°$), the spectral lines on both sides would cover one another. In practice, the plate is turned nearly 4ϕ, and by measuring the distance between the lines, the small correction to exactly 4ϕ can readily be applied.

The plate and slit must have the same distance from the rotating axis of the reflecting face of the crystal and of the plate-holder, and during exposure the crystal may, if necessary, be continually turned through a small range, and for bad crystals irregularities so eliminated. Drawings of a spectrograph for vacuum built on this principle are given, and also for the X-ray tube found most suitable.

The wave-length of Cu$K\alpha$ (the α-line of the K-series of copper) was determined to be $1537\cdot358(\pm0\cdot033) \times 10^{-11}$ cm., when the lattice constant, d, of rock-salt is taken as $2\cdot81400 \times 10^{-8}$ cm., and of calcite $3\cdot02904 \times 10^{-8}$ cm. The relation of these two constants was accurately determined for Cu$K\alpha$, Fe$K\alpha$, and Sn$L\alpha$, the wavelengths found for the last two lines being $1932\cdot39$ and $3592\cdot94$ respectively. The lattice constant found for potassium ferrocyanide was $8\cdot408 \times 10^{-8}$, instead of the value $8\cdot454$ used by Moseley, and

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the latter's wave-length tables must be diminished by 0·54% in consequence.   The following table of wave-lengths is given:

Element.	Atomic number.	$\lambda \cdot 10^{-11}$ cm.	
		$K\alpha_1$.	$K\beta_1$.
Chlorine	17	4718·70	—
Potassium	19	3733·86	3447·37
Calcium	20	3351·86	3087·89
Scandium	21	3025·26	2774·54
Chromium	24	2285·17	2081·44
Iron	26	1932·39	1753·97
Cobalt	27	1785·24	1617·58
Nickel	28	1654·67	—
Copper	29	1537·36	1389·53

This great increase of experimental accuracy is employed to test the formulæ of Sommerfeld for the difference of wave-length between the α_1 and α_2 doublet of copper in the K-series with the result, $0·373(\pm 0·005) \times 10^{-8}$, in complete agreement with theory.   Preliminary measurements of the wave-length difference of the β- and β'-lines of iron, manganese, and chromium give 3·55, 4·55, and $4·87 (\times 10^{-11}$ cm.) respectively.   The formulæ of the $K\alpha$-series given by Moseley, Sommerfeld, Debye, and J. Kroo are compared with the experimental values given in the above table, with results decidedly in favour of the formula of the last-named, the difference between the calculated and experimental results varying regularly from $-0·2\%$ for chlorine to $+0·017\%$ for copper.   F. S.

Ionisation by Canal Rays. J. STARK (*Jahrb. Radioaktiv. Elektronik*, 1918, **15**, 329—364).—A summary of the literature of the subject with a bibliography.   The account is divided into three chapters: (1) emission of electrons from metallic surfaces; (2) emission of electrons from gases; (3) emission of positive ions by canal rays.   E. H. R.

The Theory of Electrolytic Ions. X. The Conductivity of Multi-valent and Multi-stage Electrolytes. RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1919, **106**, 49—75).—A theoretical paper in which the general theory of electrical conductivity is discussed from the viewpoint of Planck's conductivity equation.   It is pointed out that the conventional use of normal solutions and _uivalent conductivities leads· to much confusion.   It is better ∴o refer all measurements to molecular quantities, no assumption being then made as to the manner in which the electrolyte dissociates.   The degree of dissociation is independent of the manner in which it takes place, and is simply defined as the ratio of the number of altered molecules to the number originally present.   The molecular conductivity quotient μ / μ_∞ has been deduced from Planck's equation for a number of different, typical· kinds of ionic dissociation.   This quotient is identical with the degree of dissociation only in the case of single-stage electrolytes, that is, of those which dissociate in one stage, whatever be the number of different

ions formed.   In the case of multi-stage dissociation, the conductivity quotient bears no relation to the degree of dissociation and is generally smaller than this.   E. H. R.

Cause of the Small Electrical Conductivity of Non-aqueous Salt Solutions. R. BEUTNER (*Zeitsch. Elektrochem.*, 1919, **25**, 97—100).—From a series of electrical conductivity measurements of solutions of salicylic acid and dimethyltoluidine in nitrobenzene solution, the author asserts that the cause of the slight conductivity of solutions of salts in non-aqueous solutions is a non-electrolytic dissociation which opposes the electrolytic dissociation.   This is supported by the observations that a solution of an acid or a base in a non-aqueous solvent has a very slight conductivity, whilst a similar solution of acid and base has a very much larger conductivity.   The conductivity of a solution of acid and base changes regularly when the concentration of the acid is changed, the base being kept constant and vice versâ.   Further, the molecular conductivity decreases with increasing dilution.   It is stated that the above observations are in keeping with the assumption that in most non-aqueous solvents an equilibrium salt $\rightleftharpoons$ acid + base exists, so that both free acid and base exist side by side with the salt.   Hence the salt, as such, has a considerable conductivity, whilst the acid and base alone have practically none.
                                                              J. F. S.

Contra-electromotive Force of Polarisation in Sulphuric Acid. ALBERT NOYES (*Compt. rend.*, 1919, **168**, 1049—1052).—The contra-electromotive force of sulphuric acid at 20° is 1·68 volts, and diminishes at first inversely as the absolute temperature.   Between 60° and 120°, it diminishes more rapidly, and above the latter temperature remains practically constant.   This may be attributed to a difference in the mode of ionisation, which is at first into H^+ HSO_4^- and then $2H^+$ and SO_4^-.   W. G.

The Potential of a Nitrogen Electrode. FRANCIS LAWRY USHER and RAMAVENKABASUBBIER VENKATESWARAN (T., 1919, **115**, 613—618).

The Chemical Process of the Lead Accumulator. CH. FÉRY (*Bull. Soc. chim.*, 1919, [iv], **25**, 223—234).—The author considers that the theory of "double sulphating" is incorrect, and that the behaviour of the lead accumulator is similar to that of a primary cell with a solid depolariser, with the difference that the negative electrode gives rise to an insoluble salt.   The reaction during normal discharging and charging is given by the reversible reaction :

$$2Pb + H_2SO_4 + Pb_2O_5 \rightleftharpoons Pb_3SO_4 + H_2O + 2PbO_2.$$
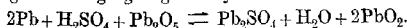
The subsulphate is a black powder and, unlike the normal sulphate, has a certain conductivity.   The higher oxide, the active material of the positive electrode, is a black, endothermic substance and a powerful oxidising agent.   W. G.

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Relationship between Electrolysis and Photolysis and Electrolytic Non-reversibility. ÉMIL BAUR (*Zeitsch. Elektrochem.*, 1919, **25**, 102—109).—The author regards photolysis as analogous to a type of electrolysis. If a substance E absorbs a light quantum it becomes polarised and a potential difference is set up. This is symbolically expressed by the equation $E + h\nu = E_{\ominus}^{\oplus}$ The conception of photolysis is compared with electrolytic action, and it is shown that the electrolysis of sodium acetate and the photolysis of acetic acid yield the same products and respectively are to be expressed by similar equations, thus: $2CH_3 \cdot COO' + 2F = C_2H_6 +$ $2CO_2$; $U^{VI} \begin{cases} \oplus\oplus + 2CH_3 \cdot COO' \\ \ominus\ominus + U^{VI} \end{cases} = C_2H_6 + U^{IV} + 2CO_2$. Glycollic acid in the presence of oxidising agents, such as ferric salts, cupric salts, or uranyl salts is converted into formaldehyde under the influence of light, and it is experimentally shown that electrolysis gives the same product. Oxalic acid is converted by light in the presence of uranyl salts into carbon monoxide and carbon dioxide, but it was found impossible to detect carbon monoxide in the products of electrolysis of oxalic acid. In the light of the present theory the author re-states with modifications the theory recently (A., 1913, i, 443) advanced with regard to the initial stages of the assimilation of carbon dioxide by plants.   J. F. S.

Disgregation of the Oxidation Products Produced on Silver Anodes in Alkaline Media. FR. JIRSA (*Zeitsch. Elektrochem.*, 1919, **25**, 146—151).—A silver anode which has been polarised in alkaline solution by direct current is temporarily depolarised by telluric acid, whilst alternating current with simultaneous polarisation by direct current makes an over-voltage on the anode impossible and depolarises permanently. When a silver anode in an alkali hydroxide is polarised by alternating current alone, it is oxidised, the current being effective only as far as its anodic component is concerned. The oxidation product, produced when an alkali hydroxide is electrolysed between silver electrodes, disperses itself throughout the solution as a colloidal suspension. When direct current is employed the suspension is Ag_2O_2, but if the solution of alkali contains telluric acid the suspension produced consists of Ag_2O_3; with alternating current the oxide Ag_2O is produced.
J. F. S.

Size of Particle, Solution Tension, and Sintering. E. PODSZUS (*Zeitsch. Elektrochem.*, 1919, **25**, 100—101).—A theoretical paper, in which a paper by Kohlschütter and Vuilleumier (this vol., ii, 9) is criticised.   J. F. S.

An Explanation of Space-filling Numbers. RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1919, **106**, 46—48).—It has been shown (this vol., ii, 212) that, for a number of univalent inorganic cations, the space-filling number ψ increases regularly with the number of

atoms in the ion. The space-filling number is a ratio of two volumes, that is, of the absolute volume of the ion, ϕ, to the ionic volume V_0 calculated additively from the usual atomic volumes of the constituent atoms. Since then the ratio increases as the number of atoms increases, it follows that ϕ increases at a greater rate than V_0, that is to say, ϕ increases more rapidly than it would do if it were an additive quantity. This can only be explained on the assumption that, when the atoms combine, a certain amount of interstitial space is included in the molecule, with the result that the ratio of the absolute volume of the molecule to the volume of its "sphere of influence" gradually increases as the molecule becomes more complex.   E. H. R.

Deduction of Cryoscopy from the General Laws of Solubility. ALBERT COLSON (*Compt. rend.*, 1919, **168**, 1047—1049). —A mathematical discussion, in which the author, starting with his law of solubility, deduces Raoult's law.   W. G.

High Temperature Researches. XII. The Measurement of Vapour Tensions at Very High Temperatures with some Observations on the Solubility of Carbon in Metals. OTTO RUFF and BERNHARD BERGDAHL (*Zeitsch. anorg. Chem.*, 1919, **106**, 76—94).—A new method has been devised for measuring the vapour pressures of metals at high temperatures and for the determination of their boiling points. The method consists in observing the gradual loss of weight occurring whilst the metal is exposed to a gradual, uniform rise of temperature to beyond its boiling point. The loss of weight is plotted against the temperature, and from the curve so obtained the boiling point is estimated. Before the boiling point is reached the curve is approximately logarithmic, and beyond this point becomes linear, but the change at the boiling point is not as sharp as might be expected. For the determinations, a small quantity of the metal, about 0·5 gram, is heated in a very small crucible of quartz or carbon. The crucible is suspended from a specially designed spring balance, by which the loss of weight is observed, and hangs inside a resistance furnace which can be evacuated and filled with an indifferent gas at any desired pressure, which is recorded by a manometer. Special provision is made to ensure a uniform rate of rise of temperature. The following results are recorded for the boiling points: mercury. 357°; cadmium, 785°; zinc, 930°; arsenic, 568°; antimony. 1330°; bismuth, 1490°; lead, 1555°; tin, 2270°; copper, 2305°; silver, 1950°; gold, 2600°. The results are compared with those of other observers, and in the cases of mercury, zinc, and cadmium, for which metals the older measurements are considered to be fairly trustworthy, the agreement is very satisfactory. The results for the vapour pressure of mercury agree well with those of Ramsay and Young (T., 1886, **49**, 453) at temperatures near the boiling point, but at lower temperatures the divergence is considerable. The new method appears to be more accurate near the boiling point.

When the measurements were made in carbon crucibles, the metal became saturated with carbon, and it was possible to estimate the solubility of carbon in the metals antimony, bismuth, lead, tin, copper, silver, and gold. In all cases the solubility was found to be too low to influence the boiling-point determinations. The solubility is highest in lead (0·094% at 1555°) and antimony (0·094% at 1327°), and in the other metals little more than a trace of carbon is dissolved.   E. H. R.

Vapour Tensions of the Metals. J. W. RICHARDS (*J. Franklin Inst.*, 1919, **187**, 581—598).—A theoretical discussion on the vapour pressures of liquid and solid metals in connexion with Trouton's rule and Richards' rule. The many equations for expressing vapour pressure as a function of the temperature are discussed. Tables are given of vapour pressures and the latent heats of vaporisation of some forty-three elements, in the former case for the solid at 0° and at the melting point; and the equations for calculating the vapour pressure at any temperature are given for both the solid and liquid. The practical significance of the vapour pressure is indicated in (1) the distillation of metals (Parkes', desilverisation process), (ii) loss of zinc in brass melting, (iii) loss of metal as fumes, (iv) sherardising and calorising, and (v) vapour losses during electrolysis.   J. F. S.

A New Laboratory Fractionating Column and the Measure of its Efficiency. M. H. ROBERT (*Compt. rend.*, 1919, **168**, 998—1001).—The column is really a double one. The lower column is an ordinary bulb fractionating column with beads, but it is surrounded by a glass vacuum jacket, which is highly evacuated. Above this column and sealed on to it is another simple fractionating column, surrounded by an outer jacket through which air is caused to circulate, and on top of this is the still-head. The column gave very satisfactory results with mixtures of alcohol and water, acetic anhydride and acetic acid, benzene and toluene, in the extraction of hexahydrotoluene from essence of Borneo, and in the fractionation of light petroleum. Using the formula $E = (a-b)/v$, and applying it to the benzene–toluene mixture, where v is the amount of benzene in the original mixture and a and b are the amounts of benzene and toluene in the first half of the distillate, the efficiency of the column was found to be 0·94 as against 0·73 for a Vigreux column and 1·0 for a perfect column.   W. G.

Direct Determination of the Temperature Exponent in the Equation of State of Fluids. E. ARIÈS (*Compt. rend.*, 1919, **168**, 930—933).—Knowing the values of T_c, P_c, and of the vapour pressures as well as the volumes v_1 and v_2 at a given temperature, the author has determined the value of n in the equation $(v_1 - v_2) = RT_c \tau (\gamma_1 - \gamma_2)/8P_c \tau^{n+1}$, for each of the seven substances for which the formula was obtained (compare this vol., ii, 184). The accuracy of these determinations has been tested by calculating the

variations of $(v_1 - v_2)$ with temperature and comparing the results against those observed by Young. The agreement is good. The values obtained for n increase by $0\cdot04$ for each increase of three atoms in the molecule of the substance, and there is an indication that the value of n for diatomic and triatomic substances must be close to but just greater than unity, that is, between 1 and $1\cdot06$.

W. G.

The Theory of the Gasification Process. [Producer Gas.] WA. OSTWALD (*Chem. Zeit.*, 1919, **43**, 229—231).—Three fundamental thermo-chemical equations represent the changes occurring in a gas producer: (1) $C + O_2 = CO_2 + 97\cdot6$; (2) $C + 2H_2O = CO_2 + 2H_2 - 18\cdot8$; (3) $C + CO_2 = 2CO - 38\cdot8$. If the carbon is utilised in these three changes in the relative proportions a, b, and c respectively, the complete process may be represented by the equation $(a + b + c)C + aO_2 + 2bH_2O = (a + b - c)CO_2 + 2bH_2 + 2cCO + 97\cdot6a - 18\cdot8b - 38\cdot8c$. Only two of the quantities a, b, and c are independent variables, and any desired values are readily represented by means of triangular co-ordinates after the manner introduced by Gibbs. Any point in the diagram may be represented by the equation as above. The values of a, b, and c can readily be determined from an analysis of the gas produced. The area of the triangle of reference is divided into two regions: (1) a region of combustion and gasification, and (2) a region of gas regeneration. Illustrations are given of the respective situations in these regions of the various technical gas mixtures. The author shows how isothermals or isocalorics are to be diagrammatically represented, and how an isocaloric solid may be constructed in any given case. The diagrams enable the thermo-chemical and volumetric characteristics of the process under any given circumstances to be readily ascertained, and to determine the effect of alteration of working on the course of the reactions, the coal consumed, the heating value of the gas obtained, etc. J. S. G. T.

Critical Temperatures of Solution in Aniline of the Principal Hydrocarbons occurring in Light Petroleum. G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, **168**, 1111—1114).—The temperature measured was in each case that above which the mixture of aniline and hydrocarbon was homogeneous, no matter what its composition. The hydrocarbons examined were those occurring in light petroleum, b. p. below 150°. The straight chain aliphatic hydrocarbons had practically the same critical temperature of solution, 71°, regardless of their molecular weight. Similarly, the β-methyl hydrocarbons all had a critical temperature of solution of about 74°. The cyclic hydrocarbons, *cyclo*hexane, etc., had critical temperatures very much lower than those of the corresponding straight chain hydrocarbons, and again the substitution of a methyl group had a marked effect. For isomeric hydrocarbons, the critical temperatures and the densities varied in an inverse ratio. W. G.

Density and Temperature. W. HERZ (*Zeitsch. Elektrochem.*, 1919, **25**, 145—146).—A theoretical paper in which the change of density in homologous series with temperature change is considered. It is shown that whilst the density of the members of homologous series at low and medium temperatures can show both a rising and a falling density with increasing number of carbon atoms, at high temperatures, near the critical point, the density increases regularly with increasing number of carbon atoms. The ratio of the densities of two members of an homologous series increases regularly with increasing temperature.   J. F. S.

Regularities in the Magnitudes of Molecular Volumes. FRITZ EPHRAIM and EDUARD MICHEL (*Helv. Chim. Acta*, 1919, **2**, 266—276).—A further discussion on molecular volumes and the percentage contraction on the sum of the constituent atomic volumes (compare A., 1917, ii, 535). Tables are given showing the percentage contraction, calculated according to the equation $c = \text{mol. vol.} \times 100 / \Sigma$ at. vol., for compounds of the alkali metals with most of the atoms or radicles, F, Cl, Br, I, O, OH, SO_4, SeO_4, NO_3, ClO_3, ClO_4, IO_3, IO_4, MnO_4, the necessary data and the authorities being quoted in another summary. Comparing the compounds with a fixed negative part, the percentage contractions are very similar, the cæsium haloids exhibiting the only abnormally great contractions. Comparing the various salts of one metal, however, great variations appear, fluorides showing contractions of about 62% and iodides about 30%. In spite of the uncertainty of much of the data, sufficient regularities are revealed to make it worth while to pursue such a line of inquiry further.   J. C. W.

Standard Substances for the Calibration of Viscometers. E. C. BINGHAM and R. F. JACKSON (*Bull. Bureau of Standards, U.S.A.*, 1918, **14**, [1], 59—86).—As liquids of greater viscosity than water, solutions of sucrose and mixtures of ethyl alcohol and water are suitable and convenient for use in calibrating viscometers. The viscosities of ethyl alcohol–water mixtures have been determined by several observers, with fairly concordant results, but the accuracy of existing data relating to sucrose solutions has been questioned. In the present work, the viscosities of 20% and 40% solutions of sucrose (by weight) were determined at temperatures from 0° to 100°, and that of a 60% solution from 10° to 95°, with results generally somewhat higher than those obtained hitherto. Existing data relating to the viscosity of water were also reviewed and corrected, the viscosity and fluidity being calculated for every degree from 0° to 100°. In discussing the relative merits of absolute and specific units for expressing viscosity, the centipoise (cp., the one-hundredth part of the *C.G.S.* unit) is favourably considered. By the use of this unit, the absolute and specific viscosities of a liquid are practically the same, provided that water at 20° be taken as the standard. The most probable value for the viscosity of water at 20° was found to be 1·005 cp.
                                W. E. F. P.

Occlusion of Hydrogen by the Metallic Elements and its Relation to Magnetic Properties.

DONALD P. SMITH (*J. Physical Chem.*, 1919, **23**, 186—202).—A theoretical paper in which the literature on the occlusion of hydrogen by metals is discussed. It is shown that the alloys produced when hydrogen is occluded by metals are to be sharply distinguished from other types of binary hydrogen compounds (KH, SbH$_3$), and that these and the hydrogen-occluding metals occupy definite sharply divided regions of Werner's periodic table. The power of occluding hydrogen is compared with the magnetic properties of the metals, and it is shown that elements with a specific magnetic susceptibility greater than 0.9×10^{-6} at the ordinary temperature occlude hydrogen strongly, whilst those with a smaller susceptibility do not occlude hydrogen. Possible exceptions to this generalisation are copper, rhodium, and thorium. Hence it is concluded that the capacity of a metal to occlude hydrogen in large amounts is restricted to those of strongly magnetic character. A fairly comprehensive bibliography of the occlusion of hydrogen by metals is appended to the paper.   J. F. S.

The Surface Condensation (Adsorption) of Water-vapour and Gases and the Errors in Weighing arising Therefrom.

K. SCHERINGA (*Pharm. Weekblad*, 1919, **56**, 94—107).—A review of the literature bearing on this subject. The author concludes that errors in weighing due to the true adsorption of water vapour or air on the surface of the most commonly occurring substances may be neglected.   W. S. M.

Adsorption of Electrolytes by Charcoal.

PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1919, **94**, 240—260).—All salts, acids, and alkalis are adsorbed by charcoal, the anions and cations being adsorbed in equivalent amounts. Iodides, cyanides, and aluminium trichloride showed a slight difference in the adsorption of anions and cations, which is apparently not due to the actual process of adsorption. The adsorbability of a salt is determined by that of its component ions. Anions are adsorbed in the order $SO_4 < HPO_4$, $Cl < Br < NO_3 < I < CNS < OH$, and cations in the order K, Na, NH$_4$ < Ca, Mg < Zn < Cu < Al < H. A strongly adsorbable ion will supersede one possessing a lower adsorbability.   J. C. D.

Adsorption by Precipitates. I.

HARRY B. WEISER and J. L. SHERRICK (*J. Physical Chem.*, 1919, **23**, 205—252).—The amount to which the following anions, chloride, bromide, iodide, chlorate, permanganate, nitrate, nitrite, cyanide, thiocyanate, ferrocyanide, and ferricyanide, are adsorbed by barium sulphate has been determined. Barium sulphate was precipitated by mixing a solution of sodium sulphate with solutions of barium salts of the various acids yielding the above-named anions, and the precipitate analysed. One hundred gram-mols. of barium sulphate adsorb

0·056 equiv. ions, I′; 0·220, CNS′; 0·310, CN′; 0·831, Br′; 1·760, Cl′; 2·695, Fe(CN)$_6$^{III}; 2·847, MnO$_4$′; 5·837, ClO$_3$′; 7·467, NO$_2$′; 8·482, NO$_3$′; 13·201, Fe(CN)$_6$^{IV}. In the case of the chlorate and permanganate ions, the adsorption is less when an excess of sodium sulphate is used in the precipitation. Changes in the conditions of precipitation affect the amount of adsorption, but not the order in which the ions are adsorbed. The observed order is not in accord with Schulze's law, although the quadrivalent ferrocyanide ion is most strongly adsorbed; but there are four univalent ions more strongly adsorbed than the tervalent ferricyanide ion, and there is a wide variation in the amounts of univalent ions adsorbed. Determination of the order of the ions by direct analysis of the adsorbing phase is preferable to deducing the order from coagulation data, since the former method is superior in accuracy. It is probably inaccurate in any case to assume that the ion with the same charge as the colloidal particles has no effect in determining the critical coagulation of the colloid by electrolytes. It is more probable that the relatively small effect of the ion with the same charge as the colloid may be lost sight of altogether, because of the errors inherent in the experimental method. The order of adsorption of anions by barium sulphate is the reverse of that deduced from Hofmeister's data (*Beitr. chem. Physiol.*, 1904, 5, 27) on the coagulation of albumin by electrolytes. The adsorption by charcoal and hydrated ferric oxide is more nearly what it is with barium sulphate. The adsorption for ions by a given adsorbent is controlled by the nature and valency of the ion. With ions of the same general character, the specific character of the adsorption is not very pronounced, and the valency factor predominates. Thus nitrate and nitrite ions are adsorbed to nearly the same extent, and among the cyanogen derivatives the order Fe(CN)$_6$^{IV}>Fe(CN)$_6$^{III}>CN′, CNS′ is observed. Nitrates are adsorbed more than chlorates and chlorides, an observation in keeping with analytical practice. Colloidal solutions of barium sulphate are usually positive, due to strong preferential adsorption of barium ion.   J. F. S.

The Congo Dyes and Adsorption as the Preliminary Phase of Chemical Union. E. WEDEKIND and H. RHEINBOLDT (*Ber.*, 1919, **52**, [B], 1013—1021. Compare Wedekind and Rheinboldt, A., 1914, ii, 626).—The behaviour of the blue solution obtained by treating Congo-red with acids towards various colloids has been examined; it is found that acid gels which are free from electrolytes (silicic acid, metastannic acid, titanic acid, tungstic acid, molybdic acid, vanadic acid) do not adsorb the Congo-dye acid and do not cause any change in colour on heating; basic gels, on the other hand (oxides of zirconium, thorium, aluminium, lanthanum, zinc, glucinum, iron, and chromium), adsorb the dye acid and, when heated, assume the red colour which is characteristic of the salts. It appears probable that the Congo-acid belongs to the weakest class of acids, and that aqueous solutions of Congo-

red, in consequence of hydrolysis, always contain a greater or less amount of the red, azoid, free Congo-acid, which is transformed by hydrogen ions into the blue, insoluble isomeride. The adsorption of the Congo-acid is attributed to the formation of a primary adsorption compound of the free blue acid, which when warmed or preserved becomes converted (probably through the red acid) into a complex salt of acid and base. The phenomenon thus gives an experimental confirmation of the hypothesis that, particularly in heterogeneous systems, chemical action is preceded by the production of an adsorption compound.

Similar behaviour is observed with other dyes, such as benzopurpurin 4B, benzopurpurin 10B, naphthalene-red, benzo-orange R, Congo-corinth G, and Congo-corinth B.   II. W.

Osmotic Pressures Derived from Vapour Pressure Measurements: Aqueous Solutions of Cane-sugar and Methyl Glucoside. THE EARL OF BERKELEY, ERNALD G. J. HARTLEY, and C. V. BURTON (*Phil. Trans.*, 1919, [*A*], **218**, 295—349).— The compressibility of solutions of sucrose and α-methyl glucoside has been determined in a series of concentrations at the temperatures 0° and 30°. In general, the method and apparatus adopted is similar to that used in the case of calcium ferrocyanide (A., 1909, ii, 126). The glass containing tubes, previously used, are, however, replaced by metal tubes fitted with a number of plate-glass windows, and the piezometer is divided into two limbs, thus providing for more rapid temperature adjustment. The apparatus was tested with water and mercury, and for these substances the following results were obtained: mercury, at 0°, mean relative coefficient of compressibility between 1—101 atms., 0.169×10^{-5}; at 1.8°, mean relative coefficient between 1—110 atms., 0.171×10^{-5}; at 29.5°, mean relative coefficient between 8—150 atms., 0.165×10^{-5}. Water at 0.12°, absolute coefficient of compressibility between 17—48 atms., 5.085×10^{-5}; at 30.01°, absolute coefficient between 17—48 atms., 4.458×10^{-5}. In the case of sucrose at 0°, compressibility coefficients were obtained ranging from 4.391×10^{-5} for a solution containing 180 grams of sucrose per litre over the pressure range 0—20 atms., to 2.235×10^{-5} for a solution of 215.4 grams of sucrose in 100 grams of water over the pressure range 10—27 atms. At 30°, values were obtained varying from 3.335×10^{-5} for a solution of 420 grams of sucrose per litre over the pressure range 0—27 atms. to 2.205×10^{-5} for a solution of 243 grams of sucrose in 100 grams of water over the pressure range 88—116 atms. In the case of α-methyl glucoside at 0°, a solution of 23 grams in 100 grams of water gave the coefficient 4.078×10^{-5} over the pressure range 17—48 atms., and a solution of 92 grams in 100 grams of water gave the coefficient 2.893 over the pressure range 0—44 atms. At 30°, for the same solutions, the values 3.848×10^{-5} over the range 20—31 atms. and 2.979×10^{-5} over the range 24—75 atms. were found respectively. Vapour-pressure determinations of solutions of sucrose, α-methyl glucoside,

and sulphuric acid have been made at 0° and 30° in an apparatus previously described (A., 1906, ii, 599). The possible sources of error in the method of determination are discussed at some length, and in the actual experiments these are avoided or corrected in the results. Very full tabulated results are given for the three substances measured, and from the results the osmotic pressure is calculated and compared with the experimentally determined value. The calculations are made by means of the expression

$$P = \log_e[l_0/l_1 - (l_0/l_1 - 1)\pi_0/B] \times RT/s,$$

where P is the osmotic pressure, s is the mean specific volume over the range $1 - (1 + P)$, l_1 and l_0 the loss of weight of the solution and solvent respectively, ρ_1 and ρ_0 the corresponding vapour densities, $\pi_{v'}$ and π_0 the corresponding vapour pressures, B the barometric pressure, $\pi_{v'}$ and π_0' the observed vapour pressures, and $[l_0/l_1 - (l_0/l_1 - 1)\pi_0/B] = \rho_0/\rho_1 = \pi_0'/\pi_{v'}$. The values previously published for calcium ferrocyanide (loc. cit.) are recalculated to allow for the "Burton correction," that the volume of the air entering the liquid is slightly different from that leaving it.

J. F. S.

The Experimental Investigation of Crystal Structure by means of X-Rays. R. GROSS (Jahrb. Radioaktiv. Elektronik, 1918, **15**, 305—329).—A useful account is given of the methods which have been developed for investigating crystal structure by means of Röntgen rays. The methods described are the Bragg reflexion method, the Laue photographic method, and the Debye-Scherrer method, by means of which a crystalline powder can be examined in place of a well-developed crystal. The results which have been obtained by the last method are particularly important, as they show that substances formerly considered to be amorphous are in reality crystalline. Thus it was found that soot has essentially the same structure as graphite, and it becomes necessary to revise our opinions of the solid state. Probably there are no true amorphous solids, only crystals and liquids with varying degrees of viscosity up to the high viscosity of the glasses. E. H. R.

Kineto-electro-magnetic Theory of Crystals. J. BECKEN-KAMP (Verh. Physik. Med. Ges. Würzburg, 1918, **45**, 135—163; from Chem. Zentr., 1919, i, 273).—The previously described models of the constitution of the atom are reviewed and Bohr's theory is extended. The helium atom must consist of four positive nuclei which, by reason of mutual repulsion, occupy the corners of a regular tetrahedron. If each tetrahedron face contains the path of an electron, the four normals constitute magnetic axes which form an astatic system, that is, one in which no external magnetic action is exhibited at a distance. The atom itself is electrically neutralised. The lines connecting the centres of gravity of atoms united by valencies form polar electric axes. In a homogeneous regular crystal, the chemical molecules appear to be invariably arranged in a four-fold cubic lattice, the latter consisting of four

interlocked simple cubic lattices. In each of these, the electric axes of all molecules are directed towards similar tetrahedra normals. In homogeneous regular crystals, therefore, the electric axes of the chemical molecules form an astatic system. The crystalline metals, copper, silver, and gold, as well as lead and aluminium, have, accordingly, monoatomic molecules, crystalline carbon a diatomic molecule, since in the first cases the atoms are arranged in one, in the second instance in two, four-fold cubic lattices. According to this hypothesis, arsenic, antimony, bismuth, and tungsten have tetra-atomic molecules in the crystalline state. In other crystals, the astatic system may be built in two ways (two parallel and opposite axes or two axes intersecting at 120°), or in accordance with the four directions of the tetrahedra normals. This theory differs from that of Bohr, since the valency is regarded from a uniform principle, the astatic arrangement of the paths of the electron, and Bohr's axioms are deduced from general or electromagnetic laws.

H. W.

Recrystallisation in Metals. G. Tammann (*Nachr. K. Ges. Wiss. Göttingen*, 1918, 1—11; from *Chem. Zentr.*, 1919, i, 321—322. Compare A., 1918, ii, 447).—During the cold working of metallic castings, planes are developed in the crystallites in which the neighbouring portions of the crystallite displace one another. In this manner, a fluid structure is attained which greatly affects the properties of the casting, particularly with regard to elasticity. The original structure returns on heating, and also the original properties. The cause of recrystallisation lies in the formation of minute new crystallites in the débris of the crystallites of the cold-worked metal; these increase very slowly at the temperature of actual commencement of the process, but with increasing rapidity as the temperature rises. If the temperature is increased in steps, each increase is accompanied by enlargement of the granules, which speedily ceases, but recommences with each new rise in temperature. An attempt is made to explain the phenomena of recrystallisation on the following lines. Two crystals in contact can only be in equilibrium with one another when crystallographically-equivalent lattice planes of both crystals lie in one plane at the surface of contact; the two space lattices must either form a single lattice or the plane of contact must be a twin plane. The two lattices must occupy a definite position with respect to one another. If one or other of these conditions is not fulfilled, new net planes of intermediate orientation are formed at the plane of contact (that is, recrystallisation begins) as soon as the temperature is raised sufficiently for appreciable change in position of the atoms or molecules in the lattice to occur. Since it is highly improbable that the contact of two crystals will occur in such a manner that a net plane of each crystal lies in one plane, recrystallisation will almost always take place at the meeting point of two crystallites. Twin formation shows that the contact of two crystals in a common plane of symmetry does not disturb the equilibrium. In twin formation,

the plane is not formed by the accidental meeting of two growing crystals, but is due to the growth of each. Twin crystals may consequently be expected to be frequently formed during recrystallisation, but the degree will vary with different metals.

Recrystallisation commences with tin after half an hour's heating at 45°; at 150°, the new particles are still relatively small. Lead behaves very similarly. With zinc, recrystallisation is distinctly evidenced at 75° by the formation of relatively large crystallites; the size of the latter decreases with increase of temperature up to 250°, and then increases, slowly at first, more rapidly from 350°. The particles are smallest between 150° and 300°. For aluminium, the minimum occurs between 300° and 500°. Observations are also recorded on rolled copper and impure tin. The unusually marked dependence of the size of the particles after recrystallisation on the degree of deformation of iron is readily interpreted by the author's hypothesis.   H. W.

Eutexis and Dilute Solutions. ALB. COLSON (*Compt. rend.*, 1919, **168**, 942– 944. Compare this vol., ii, 186).—Starting with the law of solubility (1), $425L = T(V + \epsilon)i\, dC/dT$, the volume V of the solvent, which contains 1 mol. of the solute in saturated solution, increases with cooling when $L>0$. It attains a minimum when L changes sign. At the eutectic point, it reaches a maximum, where it remains constant, and at the same time T and C remain constant. In other words, the solution maintains a constant composition, which is the same as that of the solid deposited. If to such a solution at a temperature equal or inferior to the eutectic temperature. Te, some of the solvent in the solid state is added, it remains in that form until the temperature rises above Te. The solubility of the solvent in the solution may be expressed by (2) $425L' = T(V' + \epsilon')i'\, dC'/dT$, and $dC'/dT = -dC/dT$. In other words, equation (1) gives the saturation of a substance A in a substance B, whilst equation (2) is relative to the saturation of B in A. The point of intersection of the two curves gives the eutectic point.   W. G.

Estimation of the Size and Internal Structure of Colloidal Particles by Means of Röntgen Rays. P. SCHERRER (*Nachr. Ges. Wiss. Göttingen*, 1918, 96—100; from *Chem. Zentr.*, 1919, i, 322 –323).—The method of Debye and Scherrer (*Physikal. Zeitsch.*, 1916, **17**, 277) has been applied to the determination of the size and structure of typical organic and inorganic colloids. Two cases are possible, depending on the presence or absence of crystalline structure in the single colloid particle. In the former case, numerous interference figures are to be expected in the Röntgen photographs arranged in a manner characteristic of the space lattice. The position of the interference figures does not depend on the magnitude of the single crystals, but on its breadth. In the absence of crystalline structure, one or two very flat maxima in the region of the incident Röntgen ray are to be expected, and

it is then difficult to deduce evidence as to the internal arrange-
ment of the atoms.   Silver and gold particles are found to be
crystalline and to show precisely the same space lattice as the
macroscopic gold crystals.   The size of the particles agrees with
that found by other methods.   Even in the smallest gold particles,
which are much too small to be observed with the ultramicroscope,
the characteristic space lattice is observed.   Old specimens of silicic
acid and stannic acid gels exhibit well-marked crystalline inter-
ference figures in addition to the characteristics of amorphous sub-
stances, and probably represent substances which are at the point of
crystallising.   Typical organic colloids (albumin, gelatin, casein,
cellulose, starch, etc.) appear to be amorphous; the colloid particles
therefore probably consist of individual molecules or of groups of
irregularly orientated molecules.   H. W.

Colour of Colloids. III. and IV. WILDER D. BANCROFT (*J.
Physical Chem.*, 1919, **23**, 154—185, 253—282. Compare this vol.,
ii, 102, 187).—Theoretical papers in which the discussion com-
menced in the previous papers is continued. III deals with the
effects produced by reflection from natural objects and its influence
on visibility. In IV the influence of interference and diffraction
of light is considered.   J. F. S.

**Influence of Substitution in the Components of Binary
Solutions Equilibria. XVII. Binary Solutions Equilibria
of Diphenylamine with Phenols and their Derivatives.**
ROBERT KREMANN and RUDOLF SCHADINGER (*Monatsh.*, 1919, **40**,
35—56. Compare A., 1918, ii, 68, 69; this vol., ii, 15, 55, 143).—
Melting-point curves have been constructed for the binary systems
formed between diphenylamine on the one hand and α-naphthol,
β-naphthol, pyrogallol, or one of the three dihydroxybenzenes on
the other. In no case is a compound formed between the com-
ponents, but only simple eutectics.   This is attributed to steric
influences and to a diminution of the heteropolarity. The three
binary systems formed between diphenylamine and the three nitro-
phenols also yield only simple eutectics and no compounds. Picric
acid and diphenylamine form an equimolecular compound.·   ·
                                                            J. F. S.

**Influence of Substitution in the Components of Binary
Solutions Equilibria. XVIII. Binary Solutions Equilibria
between Nitrosodimethylaniline and some Amines.** ROBERT
KREMANN and OTTO WIK (*Monatsh.*, 1919, **40**, 57—79. Compare
preceding abstract).—Melting-point curves have been constructed
for the binary mixtures formed between nitrosodimethylaniline and
α-naphthylamine, the three phenylenediamines, acetamide, benz-
amide, pyridine, quinoline, and acridine. It is shown that a com-
pound, m. p. 84°, is formed between two molecules of nitroso-
dimethylaniline and one molecule of α-naphthylamine; *m*-phenylene-

*diamine and *p*-phenylenediamine each form compounds with two molecules of nitrosodimethylaniline, whilst *o*-phenylenediamine forms an equimolecular compound, m. p. 99°. Two molecules of nitrosodimethylaniline form compounds with one molecule of acetamide and benzamide respectively. One molecule of nitrosodimethylaniline combines with four molecules of pyridine, m. p. 4·3°, whilst in the case of acridine, three compounds were formed consisting of nitroso-compound and acridine in the molecular ratios 2:1, 3:2, and 1:1. In the case of quinoline, no compounds are indicated.   J. F. S.

Investigations on Carbonate- and Chloride-Fusions. Paul Niggli (*Zeitsch. anorg. Chem.*, 1919, **106**, 126—142).—The equilibrium conditions in the system $Na_2O-K_2O-CaO-CO_2$ have been studied between 600° and 1000° in an atmosphere of carbon dioxide at atmospheric pressure. The two binary systems $Na_2CO_3-CaCO_3$ and $K_2CO_3-CaCO_3$ have previously been dealt with (A., 1916, ii, 211). The other binary system has now been studied. Sodium and potassium carbonates form a continuous series of mixed crystals, the minimum point on the curve lying at 712° with about 46 mol. % of potassium carbonate. Mixtures of sodium and potassium carbonates containing 50 mol. % of calcium carbonate behave as binary mixtures of the two double salts $Na_2Ca(CO_3)_2$ and $K_2Ca(CO_3)_2$ below 850°, but above this temperature the salts readily lose carbon dioxide. The double salts form a continuous series of mixed crystals. Mixtures of the three carbonates containing less than 50 mol. % of calcium carbonate behave up to 900° under one atmosphere of carbon dioxide as a ternary system. The equilibrium diagram is given in the form of a triangle with the three simple carbonates as the corner constituents.

In the course of the investigation of the system $Na_2Cl_2-Na_2CO_3-CaCO_3-CaCl_2$, two binary systems have been examined. The examination of the system $CaCl_2-CaCO_3$ offers great experimental difficulties. With a large proportion of calcium carbonate, the melts become very viscous at about 700°, and the cooling effects are uncertain. Sometimes, just previous to crystallisation, an emulsion appears to be formed. Formation of oxychloride is almost unavoidable. With 30 mol. % of calcium carbonate, there is a eutectic at about 622°. The system $Na_2Cl_2-Na_2CO_3$ has a eutectic point at 640°. The examination of the ternary system $Na_2Cl_2-Na_2CO_3-CaCO_3$ also offered difficulties on account of the viscous nature of the melts and of the small thermal effects. Two characteristic arrest points were found, at 690° and 640°. The results are shown on a triangular diagram with Na_2Cl_2, Na_2CO_3, and $CaCO_3$ as the corner constituents. The petrological significance of the results of the investigations is discussed.   E. H. R.

The Propagation of Flame in Mixtures of Acetylene and Air. Walter Mason and Richard Vernon Wheeler (*T.*, 1919, **115**, 578—587).

Calculation of Temperatures of Explosion. A. V. Blom[*]

(*Z. ges. Schiess. u. Sprengstoffw.*, 1916, 11, 219—221; from *Chem. Zentr.*, 1919, i, 268).—The maximum temperature obtained during explosion may be calculated from the formula: (1) $dQ = C' \cdot dt$, where Q is the heat of combustion and is determined calorimetrically or calculated from thermochemical data, and C' the true molecular specific heat at constant volume. From the values for the specific heat of polyatomic gases obtained during recent years (the calculations of temperature, particularly for triatomic gases and the older linear formulæ, are useless), the following functions (2) for C' are obtained: H_2, $C' = 4.70 + 0.90 \times 10^{-3}t$; O_2, N_2, CO, $C' = 4.90 + 0.90 \times 10^{-3}t$; CO_2, $C' = 7.98 + 2.44 \times 10^{-3}t$; H_2O, $C' = 3.84 + 4.68 \times 10^{-3}t$. $C' = \alpha + \beta t + \gamma t^2 + \delta t^3 + \ldots$ (The temperature-coefficients express the mobility of the atoms in the molecule.) Using the general expression $C' = \phi(t) = \alpha + \beta t$, and substituting in equation (1), the formula $dQ = (\alpha + \beta t)dt$ is obtained, which, on integration, becomes $Q = \alpha t + (\beta/2)t^2$ (3). If the relative quantities of gases formed by explosion are [H], [N], [O], [CO], [CO$_2$], and [H$_2$O], the following coefficients are derived from formula (2):

$$\alpha = 4.70[H] + 4.90\{[N] + [O] + [CO]\} + 7.98[CO_2] + 3.84[H_2O],$$
$$\beta = 0.9\{[H] + [O] + [N] + [CO]\} + 2.44[CO_2] + 4.68[H_2O] \cdot 10^{-3}.$$

The temperature of explosion may then be calculated by substituting these coefficients in equation (3).　　　　H. W.

The Determination of the Temperatures Reached in Explosive Reactions. Henri Muraour (*Compt. rend.*, 1919, 168, 995—997).—The two indirect methods commonly used for evaluating the temperatures reached in explosive reactions require the assumption of the composition of the gas at the moment of the explosion, and according as it is assumed that methane exists at the moment of the explosion or that it is formed during the cooling, so wide differences in temperature may be obtained.

Working with powders, which gave gases rich in methane, and using an "erosion" bomb with sudden liberation of the gases, the author finds that the greater part, if not the whole, of the methane contained in the products of combustion of powders is formed during the period of cooling. Thus, then, in calculating the temperatures of explosion, the most accurate results will be obtained by reverting the whole of the methane to $CO + H_2$. As a result of this, it is shown that the temperature of explosion of powders does not increase when the density of the charge is increased.　　　　W. G.

The Thermal Decomposition of Phosphine. Max Trautz and Divacar S. Bhandarkar (*Zeitsch. anorg. Chem.*, 1919, 106, 95—125).—The rate of decomposition of phosphine into phosphorus and hydrogen has been measured manometrically in a porcelain vessel at temperatures between 845° and 956°. Above the latter temperature, the decomposition is too rapid for measurement. The

reaction is of the first order, and is the first example of a gas reaction of this order to be recorded. Only above 945°, however, is the reaction uninfluenced by the walls of the vessel, and therefore a pure gas reaction. Above this temperature, the temperature-coefficient is about 1·8, but below 945° it sinks rapidly, owing to the growing predominance of the surface reaction. By means of the theory of gas reactions, the "heat of activation" and the size of the phosphine molecule are calculated. From the value of the former quantity, it is calculated that the limit of photosensitiveness for phosphine, apart from the infra-red, lies at about 329 $\mu\mu$. This research provides the first experimental proof of the theory of gas reactions (A., 1918, ii, 151), and also confirms the opinion that a gas reaction can be freed entirely from the influence of the surface of the reaction vessel if the temperature be raised sufficiently high.

The reaction appears to be retarded by water vapour and accelerated by copper, but the differences observed scarcely fall outside the limits of error of the experiments.   E. H. R.

Catalysis. XI. The Le Chatelier-Braun Principle from the Point of View of the Radiation Hypothesis. WILLIAM CUDMORE MCCULLAGH LEWIS (T., 1919, 115, 710—712).

The Atomic Ether, Hydrogen Atom, and Planck's Energy Quantum. L. ZEHNDER (Ber. Deut. physikal. Ges., 1919, 21, 118—125).—A theoretical paper in which the author puts forward a theory of an atomic ether. This substance is supposed to be made up of spherical ether atoms which are very small in comparison with atoms of matter; they are completely elastic, and move with a velocity comparable with that of light. A sheath of ether atoms surrounds every material atom and molecule, and all matter is pervious to ether atoms, so that there is no such state as an ether vacuum. The author is of opinion that differences in velocity of ether atoms constitute many of the physical phenomena; for example, electricity is nothing but the heat of the ether, and light, percussion of the ether. The electron is made up of a definite number of ether atoms with an increased heat content. The increase of mass of an electron with increase in velocity is attributed to the carrying of more ether atoms by the electron. This theory is examined in connexion with several physical laws, and found not to be at variance with them. The hydrogen atom is supposed to be spherical, made up of a perfectly elastic nucleus surrounded by an imperfectly elastic ether sheath.   J. F. S.

Mechanical Philosophy and Surface Tension. FRED G. EDWARDS (Chem. News, 1919, 118, 270—271).—A theoretical paper in which it is shown that the difference in thermal energy of an electron inside a liquid and a free electron may be measured by the relative energies of the positive ether atom. The energy of the positive atom of free ether is 1·058 erg., and may be calculated

by the equations $U = \frac{3}{2}pv = \frac{3}{2}(5175 \times 10^{17})(1\cdot39 \times 10^{-24})$ $C.G.S.$, $U = \frac{1}{2}mC^2 = 0\cdot4C^2 \times 10^{-24}$ $C.G.S.$ From these formulæ, the velocity (C) of the ether atom is found to be $5\cdot193 \times 10^{10}$, or $3\sqrt{3} \times 10^{10}$ cm./sec. This value is $\sqrt{3}$ times the radiation velocity, that is, tan 60° times the radiation velocity, thus proving that the path of the ether atom coincides with the four edges of a regular tetrahedron. This completes the theory of an atomic ether, previously published (*ibid.*, 1919, **118**, 183), and shows that the atom does not reciprocate in a rectilinear path, which would be the hypothetical alternative motion in a dodecahedral formation with double plena. In dilute solution, the intrinsic molecular pressure of water is found to be $4\cdot51119 \times 10^{11}$ dynes, which is about forty-one times larger than the generally accepted estimate. This intrinsic pressure can be exactly determined from the heat of neutralisation, so that the unknown term dp/dT of the Clausius equation $(dp/dT = L/(T[v_2 - v_1])$ can be calculated. Further, if the Eötvös formula is accepted, the surface tension of a single molecule is obtainable with the weight of the molecule or molecular aggregate, and as the periodic specific volumes and periodic specific entropies of the elements are measurable, they can all be shown to be functions of the atomic shapes, which recur in accordance with the periodic system when the chemical atoms are assumed to be built up symmetrically with the ether atom as the tetrahedral unit.

J. F. S.

Theory of Allotropy: Allotropes and Allotropoids.

MAURICE COPISAROW (*Chem. News*, 1919, **118**, 265—266).—Allotropy is defined as the capacity of an element to exist in forms differing in the mode of their intramolecular linking; it is to be regarded as a function of the valency. From this definition, it becomes possible to deduce the number of allotropes of a given element. Univalent elements can exist in only one allotropic modification, bivalent elements in two forms: (*a*) as a molecular structure in which both valencies of the elements are fixed, (*b*) as molecular structure in which some valencies are free. In the case of tervalent elements, two allotropes are possible: (*a*) a saturated molecular structure in which all valencies are fixed, (*b*) an unsaturated molecular structure in which some valencies are free. Quadri-, quinqui-, and other multi-valent elements may exist in three allotropic modifications: (*a*) a rigid molecular form in which all valencies are fixed, (*b*) a rigid molecular form in which some valencies are free, and (*c*) a non-rigid molecular form in which some valencies are free. It thus follows that valency and the saturation or fixation of the atoms, and not the number of atoms, play the predominant part in the determination of allotropes, and consequently allotropy becomes the capacity of an element to exist in forms differing in the mode of their intramolecular structure. Molecular forms differing in the number of atoms or the distribution of linkings, but all belonging to the same type of linking, can be termed allotropoids. These molecular forms serve as the transi-

tion stage between polymorphism and allotropy, and can be compared with cryptoisomeric substances.   J. F. S.

The Hollandus Writings : a Forgery in the Second Half of the Sixteenth Century. PAUL DIERGART (*Chem. Zeit.*, 1919, **43**, 201).—A reasoned statement showing that the works attributed to Isaak and Johann Isaak, of Holland, are forgeries of a date somewhere in the second half of the sixteenth century.   J. F. S.

The Death of Scheele. LUCIANO P. J. PALET (*Anal. Soc. Quím. Argentina*, 1919, **7**, 44—48).—The author directs attention to an error widely disseminated in chemical and toxicological literature that Scheele died from the effects of the inhalation of hydrogen cyanide, which he discovered. The error seems to have arisen from the confusion of the following facts. In 1775 Scheele discovered hydrogen arsenide, and in 1782 hydrogen cyanide. In 1813 the toxicity of the latter gas was demonstrated by Gehlen, also a Swede, who died in 1815 from the effects of poisoning with hydrogen arsenide. Scheele died in 1786 of phthisis.   W. S. M.

Loosening of Fixed Glass Parts (Stopcocks, etc.) by means of Hydrogen Peroxide. SCHWARZE (*Münch. Med. Woch.*, 1918, **65**, 1327; from *Chem. Zentr.*, 1919, ii, 83).—Glass stoppers, stopcocks, etc., which have become fixed may be loosened by immersion in undiluted hydrogen peroxide solution.   H. W.

Device for Removing Plugs from Stopcocks. VERNON C. ALLISON (*J. Ind. Eng. Chem.*, 1919, **11**, 468).—The apparatus consists of a wooden vice, one jaw of which is hollowed so that it fits over the handle and presses against the wide end of the barrel of the tap, whilst the other jaw carries a pin, by means of which a steady pressure can be exerted against the narrow end of the tap. Almost any tap which has "stuck" can be loosened by using this vice.   W. P. S.

Inorganic Chemistry.

The Systems Chlorine, Hypochlorous Acid, Sodium Hypochlorite. DE MALLMAN (*Compt. rend.*, 1919, **168**, 1114—1117). —To determine the amounts of free chlorine x, chlorine as hypochlorous acid y, and chlorine as sodium hypochlorite z, in an aqueous solution containing chlorine in the three forms, the following process is recommended. The total active chlorine, a, is first determined, giving $x + 2y + 2z = a$, and if this is determined iodometrically, the mixture with potassium iodide being acidified with a known volume of $N/5$-hydrochloric acid, then the loss in acidity,

β, may be subsequently determined, and expressed in terms of chlorine gives $y+2z=\beta$. If, now, air is bubbled through a given volume of the original solution for five minutes, the whole of the free chlorine is removed, and may be estimated iodometrically, giving x, and thus the three unknowns may be determined. If sodium chloride is present, the value for x is slightly too high, a portion of the chlorine present as hypochlorous acid being carried over. As a result of numerous experiments, the author concludes that when chlorine, hypochlorous acid, and sodium hypochlorite in aqueous solution are mixed, there is produced, in reality, the reversible reaction $Cl_2 + NaOCl + H_2O \rightleftharpoons 2HClO + NaCl$.　W. G.

Existence of Polythionic Chlorides in Solutions of Sulphur in Sulphur Monochloride. G. BRUNI and M. AMADORI (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 217—228).—The cryoscopic behaviour of sulphur monochloride in bromoform solution corresponds with the formula S_2Cl_2. A mixture of sulphur monochloride and sulphur depresses the freezing point of bromoform by an amount less than the sum of the depressions produced by the two solutes taken separately. The conclusion is drawn that such a solution contains polythionic chlorides in equilibrium with their components, the divergence of the actual from the calculated depression indicating approximately the formula of the complex chloride. In bromoform solution, the highest such complex compound definitely known to be present is the tetrathionic chloride, S_4Cl_2, but chlorides richer in sulphur probably exist in solutions of sulphur in the monochloride. To the presence of these polythionic chlorides are due the formation of polythio-derivatives by the action, substitutive in character, of sulphur monochloride on organic substances, and also the fact that, in the cold vulcanisation of caoutchouc by means of sulphur monochloride, products may be formed containing sulphur in excess of the ratio $S:Cl$.　T. H. P.

The System SiO$_2$. A. SMITS and K. ENDELL (*Zeitsch. anorg. Chem.*, 1919, **106**, 143—148).—In an earlier paper (A., 1913, ii, 318), an attempt was made to explain the system SiO_2 in terms of the authors' theory of allotropy, two pseudo-components being assumed. To account for a metastable transition point, however, the system must be at least ternary, and consequently the solution put forward in the earlier paper is incorrect. An assumption of three pseudo-components is now made, of which two are assumed to be in a state of invariable equilibrium, and are treated in the equilibrium diagram as one component. The discussion is limited to the α- and β-crystobalite portion of the system, and does not deal with tridymite.
　E. H. R.

Limits of Formation of Mixed Crystals between Potassium Chloride and Sodium Chloride. R. NACKEN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1918, 192—200; from *Chem. Zentr.*, 1919, i, 77. Compare Kurnakov and Shemtschushni, A., 1906, ii, 443).—The experiments were undertaken with the

object of investigating the separation curve with greater accuracy than has yet been possible with cooling curves, which can show considerable inaccuracies due to the tardiness with which equilibrium is established in the solid phase. The method adopted was that of Day and Sosman (A., 1911, ii, 496), and the region of existence of mixed crystals was found to be considerably smaller than has been previously assumed. The critical separation temperature lies slightly below 500° (according to previous determinations, 373—405°), the composition of the maximum at about 65 mol. % NaCl. In a mixture of the two components, pure sodium chloride appears to be stable below 300°, pure potassium chloride slightly below 250°.

Investigation of the various mixtures was carried out by the aid of their refractive indices, using suitable mixtures of liquids; the latter were made up from eugenol with either oil of cinnamon or sandal-wood oil or Bergamot oil.   H. W.

Rearrangement of Acid Salts of Dibasic Acids in Aqueous Solutions into Normal (Neutral) Salts and Free Acids. II. TH. SABALITSCHKA (*Ber.*, 1919, 52, [*B*], 567—584. Compare A., 1917, i, 699, 700).—Some further experiments of a more exact nature are described, demonstrating that acid salts of dibasic acids exist in solution to a greater or less extent as a mixture of normal salts and free acids.

I. *Dialysis of Aqueous Solutions.*—The diffusates of solutions of sodium and potassium hydrogen sulphates contain quantities of free sulphuric acid which indicate that about 43% or 28·3% respectively of the acid salts have been transformed in solution into mixtures of free acid and normal salts. Similarly, the diffusate of potassium hydrogen camphorate contains an excess of the normal salt, the free acid being so slightly dissociated that it cannot diffuse so rapidly as its ion.

II. *Crystallisation.*—A 32% solution of potassium hydrogen sulphate, left at 5—10° for a few days, deposits neutral crystals. A 50% solution of sodium hydrogen sulphate (salt to water, 1:1), left at 5—10°, gives crystals consisting of Na_2SO_4 91·754%, $NaHSO_4$ 5·867%, H_2O 2·38%. A solution of potassium hydrogen camphorate, made by dissolving 5 grams of the acid in 250 c.c. of 0·1N-potassium hydroxide and evaporating to 180 c.c., deposits pure camphoric acid on cooling.

III. *Precipitation with Alcohol.*—A solution of sodium hydrogen sulphate (20 grams = 17·506 grams of $NaHSO_4$, in 50 c.c.), mixed with alcohol until a turbidity just appears (200 c.c.), gives a precipitate, during two days, of pure sodium sulphate, leaving only 4·2% of the acid salt in solution. The alcohol may be recovered easily. (Compare the experiment with the potassium salt, *loc. cit.*)

IV. *Extraction of the Acid [Organic] with Ether.*—Quantitative experiments with the camphorate are described (*loc. cit.*).
    J. C. W.

Electrolytic Dissociation of Sodium Iodide. Bror
Holmberg (*Svensk. Kem. Tidskr.*, 1918, pp. 6; from *Chem. Zentr.*, 1919, i, 211).—The author finds that the law of mass action is strictly applicable to the ionic dissociation of sodium and potassium iodides at concentrations from $1N$ to $0.05N$. The method of experiment is based on the fact that the velocity of racemisation of *l*-iodosuccinic acid is dependent on the concentration of iodine ions in the solution. H. W.

New Method for the Preparation of Ammonium Iodide.
E. Rupp (*Apoth. Zeit.*, 1918, **33**, 406, 473; from *Chem. Zentr.*, 1919, i, 10. Compare Brocksmit, A., 1918, ii, 16).—The following is the most suitable method of preparing ammonium iodide from ammonia and iodine in the presence of hydrogen peroxide. Powdered iodine (10 parts) is shaken with official hydrogen peroxide solution (60 parts) and gradually treated with ammonia solution (30 parts), when the iodine passes into solution. If necessary, hydrogen peroxide is added drop by drop until further evolution of gas does not occur and the solution is pale yellow in colour. The filtered solution is warmed on the water-bath, when it becomes colourless; after evaporation, the salt is rubbed with a small quantity of ammonia and dried. H. W.

Ammonium Silicate. II. Ammonia and Silicoformic Acid [Dioxodisiloxane]. Robert Schwarz (*Ber.*, 1919, **52**, [B], 601—606. Compare A., 1917, ii, 31).—In the experiments on the solubility of silicic acid in ammonia solutions described previously, it was doubtful whether neutralisation or merely the production of a colloidal solution had occurred. It is now shown that dioxodisiloxane, made by leading trichloromonosilane vapour into water, reacts with ammonia solution just as it does with potassium or sodium hydroxide, that is, according to the equation $Si_2H_2O_3 + 4NH_4 \cdot OH = 2(NH_4)_2SiO_3 + 2H_2 + H_2O$. The reaction is completed in about twenty minutes, and most of the silica, with which specimens of dioxodisiloxane are usually contaminated, remains as a precipitate. J. C. W.

Influence of Different Ammonium Salts on the Precipitation of Magnesium Hydroxide. E. Brunner (*Helv. Chim. Acta*, 1919, **2**, 277—279).—If the usual explanation of the influence of ammonium chloride in preventing the precipitation of magnesium hydroxide is correct, namely, that the effect is due to the mass action of the ammonium ions provided by the salt, then a less completely dissociated salt, like ammonium sulphate, would have a weaker influence. Experiments are described which prove that the reverse is the case. Under equivalent conditions, ammonia solution produces less precipitate from magnesium sulphate when ammonium sulphate is present than when the preventative is ammonium chloride, and a mixture of the two chlorides gives much more precipitate than a mixture of the two sulphates. Even in

the absence of an ammonium salt, the sulphate gives less precipitate than the chloride.

The explanation is to be found in the greater dissociation of magnesium chloride. The sulphate dissociates largely as follows: $2MgSO_4 \rightleftharpoons Mg^{..} + [Mg(SO_4)_2]''$ (compare Bredig, A., 1894, ii, 226), and therefore gives fewer magnesium ions than the chloride. The addition of ammonium sulphate depresses the normal dissociation still .further, which explains the great stability of cerbolite, $MgSO_4,(NH_4)_2SO_4,6H_2O$ (Jones and Caldwell, A., 1901, ii, 375).

J. C. W.

The Nature of Subsidiary Valencies. XXIII. Thermal Degradation of the Ammines of Zinc. FRITZ EPHRAIM (Ber., 1919, **52**, [B], 957—964. Compare this vol., 286, 287, 291).—The expected analogy between the ammines of copper and zinc has led to a study of the latter in which only a slight parallelism is observed between the two series. The following ammines have been investigated, their temperature of decomposition being placed within brackets after each number: zinchexammine chloride (57·5°), tetra-ammine (92°), diammine (not below 200°); zinchexammine bromide (62°), tetra-ammine (143°), diammine (?); zinchexammine iodide (65°), tetra-ammine (199°), diammine (?); zinchexammine nitrate (31·5°), tetra-ammine (206°), triammine (?); zinchexammine formate (−4°), tetra-ammine (51·5°), $Zn(HCO_2)_2,2\cdot5NH_3$ (63°), diammine (not below 100°); zincpentammine oxalate (18°), diammine (?); zinchexammine thiocyanate (0°), tetra-ammine (86°), the triammine possibly exists; zincoctammine benzoate (−3°), pentammine (21°), triammine (56°), diammine (not below 100°); zincpentammine sulphate (19°), tetra-ammine (98·5°), triammine (185°), diammine (?).   H. W.

Cryoscopic Study of Couples. Cadmium Bromide—Alkali Bromide. E. CORNEC and G. URBAIN (Bull. Soc. chim., 1919, [iv], **25**, 215—218).—A study of the freezing-point curves of aqueous solutions of cadmium bromide with the different alkali bromides and hydrogen bromide reveals the existence in solution of double salts of the type $CdBr_2,2MBr$, where M may be hydrogen, potassium, sodium, or ammonium.   W. G.

Cryoscopic Study of Couples. Cadmium Chloride– Alkali Chloride. E. CORNEC and G. URBAIN (Bull. Soc. chim., 1919, [iv], **25**, 218—222. Compare preceding abstract).—In the case of cadmium chloride and alkali chlorides, a cryoscopic study reveals the existence in aqueous solutions of double salts of the type $CdCl_2,MCl$, where M may be hydrogen, potassium, sodium, or ammonium.   W. G.

Lead Nitrato-Hypophosphate and Related Substances. EDMUND VON HERZ (Z. ges. Schiess. u. Sprengstoffw., 1916, 11, 365—367, 388—389; from Chem. Zentr., 1919, i, 271).—Attempts

to use phosphorus and its compounds in the manufacture of explosives have generally resulted in failure, but a highly explosive double compound, $Pb(NO_3)_2.Pb(H_2PO_2)_2$, may be prepared when lead nitrate, as source of oxygen, is mixed in the moist state with lead hypophosphite. Its rate of detonation is greater than that of mercury fulminate and approximately equal to that of lead azide. Its small energy content, or the relatively small volume of gas liberated by its decomposition (117 litres per kilo., as contrasted with 230 litres with lead azide and 314 litres with mercury fulminate), inhibits its use as initial explosive in the usual amount of charge. Its suitable sensitiveness and detonation point, its great stability, and the high temperature of its flame render it very appropriate for percussion-fuse compositions. It is prepared by adding a hot saturated solution of lead nitrate (331 grams) to a boiling saturated solution of calcium hypophosphite (170 grams), and cooling the mixture rapidly with efficient stirring, when white, crystalline lead hypophosphite separates. Two hundred and fifty grams of the latter are added with stirring to a boiling solution of lead nitrate (500 grams) in water (1·5 litres), and rapidly cooled. The double compound, dried at 40—50°, is only practically useful when it is obtained as a heavy, granular, crystalline powder; it is less suitable in the form of needles or as a felted, voluminous mass.

H. W.

New Atomic Weight Determinations. [Thorium-lead and Scandium.] O. HÖNIGSCHMID (*Zeitsch. Elektrochem.*, 1919, **25,** 91—97).—An account is given of a series of atomic weight determinations of thorium-lead and scandium. Lead from thorite was converted into chloride, and the ratios $PbCl_2 : 2Ag$ and $PbCl_2 : 2AgCl$ determined. From these experiments, the values 207·88 (one expt.) and 207·91 (two expts.) were obtained respectively. The mean value for Pb_{Th} is $207·90 \pm 0·013$, which is the highest value yet obtained for any variety of lead. Further experiments were also made by the same method with lead from three different samples of thorianite of unknown origin, but probably from Ceylon. The following mean values were obtained: (1) 207·21, (2) 206·91, and (3) 206·84 for the three samples. From the results of the investigation, the author is of the opinion that a lead isotope of atomic weight 208·1 probably exists, and that in all probability Th.-D is not absolutely stable, but has a very long average life. The general question of the origin of the various lead isotopes is discussed, and the recent work of Soddy, Fajans, and others reviewed in this connexion. It is pointed out that the whole of the atomic weight determinations of scandium have been made by the sulphate method, and that very divergent results, fluctuating between 44·1 and 45·2, have been obtained by different investigators. The author has therefore made a series of analyses of the bromide by the Richards method. The bromide was prepared by heating the oxide in a quartz tube with carbon and bromine vapour, and the product purified by sublimation in a quartz tube. The

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product was collected and treated generally in the way adopted by the author in his determinations of the atomic weights of uranium and thorium (A., 1916, ii, 484, 510). The sublimation of scandium bromide does not take place below about 1000°, at which temperature the substance has not melted. It is also found that after sublimation the quartz tube has been attacked to a slight extent by the bromide, according to the equation $4ScBr_3 + 3SiO_2 = 3SiBr_4 + 2Sc_2O_3$. The amount of the reaction is not great, and was determined by weighing the quartz tube before and after the experiments. A correction based on this action was introduced into the final calculations. For the purpose of reducing the weighings to vacuum standard, the specific gravity of scandium bromide was determined, and the value 3·910—3·913 obtained. Two specimens of scandium were used in the experiments: I, supplied by R. J. Meyer, and II, supplied by Sterba-Böhm. These specimens had been purified by different methods, and a spectroscopic examination by Haschek indicated that they were both absolutely pure—so pure, in fact, that the very persistent ytterbium line $\lambda = 3694·37$ was not present in the spectra. Specimen I gave a mean value for the atomic weight Sc = 45·105 (eight expts.), and specimen II the value Sc = 45·093 (ten expts.), the mean of the whole being 45·099 ± 0·014, a value which is rounded to 45·10, and is one unit higher than the value 44·1, at present adopted by the International Atomic Weight Committee.   J. F. S.

Blue Copper Oxide. H. E. SCHENCK (*J. Physical Chem.*, 1919, **23**, 283—285).—A mixture of copper sulphate and aluminium containing approximately 5% of copper oxide was dissolved in water and precipitated with a slight excess of sodium hydroxide, filtered, thoroughly washed, and dried at 110°. The dried precipitate was very light blue in colour, and on grinding to a very fine powder and heating first in a Bunsen flame and then in a blowpipe flame, the colour changed to a light greyish-blue with no signs of blackening. A similar mixture containing twice as much copper oxide remained blue after heating in the Bunsen flame, but showed signs of blackening when heated in the blowpipe. The view is expressed that alumina stabilises the blue oxide of copper, and that the change from blue to black is due to an agglomeration of the particles. Similar preliminary experiments were made with other oxides; these were in all cases made with 5% of the oxide to 95% of alumina; manganous oxide is pink before heating and brown after heating; cobalt oxide is white with a blue tinge, but deep blue after heating, and nickel oxide is green before heating, but yellow after heating.   J. F. S.

The Nature of Subsidiary Valencies. XX. Ammines of Cuprous and Lithium Salts. FRITZ EPHRAIM (*Ber.*, 1919, **52**, [*B*], 236—241. Compare A., 1918, ii, 313).—The author hoped to find simple rules governing the formation of ammines by the salts of univalent metals, but has met with quite conflicting conditions

in the case of silver (*ibid.*), aurous, cuprous, thallous, and lithium compounds, as may be seen from the following summary of the properties of the haloids. Lithium salts yield tetrammines, which increase in stability from chloride to iodide. The same order of stability, with smaller and smaller differences, is met with among the tri- and di-ammines, but in the case of the monoammines the order is reversed, as it is with the silver haloid triammines. Cuprous haloids form triammines of almost identical stability, whilst aurous salts only give diammines. Thallous salts, owing no doubt to the great atomic volume of thallium, do not combine with ammonia. The lack of co-ordination with the generalisations made in earlier papers is obviously due to the fact that these were made on hexammines, which the salts of univalent metals do not form at all.

The following list records the temperatures at which the vapour pressures of the ammines are 760 mm. Triammines are formed by cuprous chloride, 46·3°; bromide (pale green), 49·3°; and iodide (almost white), 50°. Diammines only are given by cuprous thiocyanate and nitrate, whilst the cyanide only forms a monoammine. (The present results differ from Lloyd's, A., 1908, ii, 847.) Tetrammines are produced by lithium chloride, 12°; bromide, 53·8° (Bonnefoi, A., 1900, ii, 478); iodide, 90·5°; nitrate, a syrup, more stable than the chloride tetrammine; chlorate, a fairly mobile liquid; and perchlorate, a solid which decomposes and liquefies at the ordinary temperature.   J. C. W.

The Nature of Subsidiary Valencies. XXII. Thermal Degradation of Ammines of Copper.

Fritz Ephraim (*Ber.*, 1919, **52**, [*B*], 940—957. Compare Ephraim and Bolle, A., 1916, ii, 104).—The present communication deals mainly with the stability of the intermediate ammines of copper, and forms the first of a series of such investigations, the theoretical discussion of which is withheld pending the accumulation of more comprehensive data.

The experiments were performed by saturating the requisite salt with ammonia at a low temperature in a bulb blown at the bottom of a small Y-tube; the temperature of the ammine was then gradually raised and maintained constant at those points at which gas was noticeably evolved until evolution of gas practically ceased, the composition of the residue being deduced from the loss in weight. In general, three cases present themselves: (1) the ammine is stable up to a definite temperature, slightly above which ammonia is rapidly evolved, and the next lower ammine is formed; (2) a continuous series of solid solutions exists between two well-defined ammines; (3) the ammine yields solid solutions initially, which are suddenly discontinued, and ammonia is rapidly evolved to the next lower stage, or, conversely, a sudden evolution of ammonia is followed by the formation of solid solutions.

Cupric chloride gives the following ammines: $CuCl_2,2NH_3$, which decomposes below 270°; $3CuCl_2,10NH_3$, formed at 105° and stable to 124°, when it yields the diammine; $CuCl_2,5NH_3$, which below

$105°$ forms solid solutions, which attain the composition $CuCl_2,6NH_3$ at about $-15°$. Cupric bromide yields $CuBr_2,2NH_3$, decomposing at about $260°$; $3CuBr_2,10NH_3$, decomposing at $155°$; $CuBr_2,5NH_3$, unstable above $116°$ and yielding solid solutions below this temperature, which have the composition $CuBr_2,6NH_3$ at about $0°$. Cupric iodide yields solid solutions of hexammine and pentammine, which have the composition of the latter at $119·5°$, when $3CuI,10NH_3$ is formed; the latter passes at $147°$ into the diammine. Copper sulphate gives a pentammine, which at about $99°$ is converted into the tetra-ammine, which slowly loses ammonia at $141·5°$, forming the diammine. Copper nitrate gives a deep blue tetra-ammine, which is converted below $15°$ into a similarly coloured hexammine and decomposes above $205°$, yielding indefinite products. Copper pentammine thiocyanate is converted into the tetra-ammine at $3°$, which is stable to $101°$, when gas is evolved and a series of solid solutions is formed up to $127°$, at which the diammine is formed; decomposition occurs above this temperature. Copper tetra-ammine acetate is converted at about $80°$ into the diammine, which decomposes at about $175°$. Copper pentammine oxalate is slowly converted into the diammine at about $46°$; the latter is stable at $170°$, but is completely decomposed at a higher temperature. Copper octammine benzoate is stable below $-3°$, at which temperature it is transformed into the hexammine; the latter decomposes with rising temperature, yielding solid solutions, which at $78°$ have the composition of the tetra-ammine; at $180°$, formation of the diammine is complete, whilst at higher temperatures the material melts and decomposes.   H. W.

Thallous Oxide. ALFRED KÖLLIKER (*Chem. Zeit.*, 1919, **43**, 231).—In this preliminary communication, the author disputes the statement occurring in the literature of the subject that "the greyish-black coating of oxide produced when the metal is exposed to air does not penetrate far into the metal, the latter reappearing when the oxide is dissolved in water." Thallium was prepared from thallium sulphate either electrolytically or by means of zinc, and it was found that the whole of the metal was oxidised in a little time. The thallous oxide formed goes completely into solution, and any of the thallium salts can be precipitated therefrom by the usual precipitants, a property which can be utilised for the separation and purification of thallium salts.   J. S. G. T.

Cerium Nitride. P. FABARON (*Ann. Chim. anal.*, 1919, [ii], **1**, 156).—When metallic cerium is heated in a closed copper tube, the oxygen of the air in the tube combines with the copper and the nitrogen with the cerium. The cerium nitride, CeN_2, formed has a greyish-black colour and is decomposed by water, yielding ammonia and cerous oxide.   W. P. S.

The Constitution of the Ferric Salts of Hypophosphorous Acid. R. F. WEINLAND and W. HIEBER (*Zeitsch. anorg. Chem.*, 1919, **106**, 15—45).—In addition to the previously known normal

ferric hypophosphite having the composition $Fe(H_2PO_2)_3$, a number of new basic compounds have now been prepared. It has also been found that ferric hypophosphite combines with other inorganic acids to form complex compounds containing both acid radicles, and many such compounds have been characterised and analysed. On account of the stoicheiometric relationships found between the different compounds, and of their singular properties, in particular of their remarkable stability, it has been concluded that the majority of the compounds contain the complex cation $[Fe_3(H_2PO_2)_6]'''$, which is very stable in character and is capable of forming salts both with hypophosphorous acid and with other inorganic acids. In this respect, the ferric salts of hypophosphorous acid are very similar to those of a number of monocarboxylic acids previously described (A., 1916, i, 314).

The normal ferric hypophosphite (3:9) is considered to have the constitution $[Fe_3(H_2PO_2)_6](H_2PO_2)_3$. The 3:8 basic salt is prepared in a pure state by mixing solutions of ferric chloride and sodium hypophosphite within certain narrow limits of temperature and concentration. It forms a loose, slightly red powder, and is given the constitution $[Fe_3(H_2PO_2)_6OH](H_2PO_2)_2,24H_2O$. This salt was used for preparing many of the following hetero-acid compounds. Other basic salts isolated contain metal and acid in the ratios 6:15, 3:7, and 3:6 respectively. The last salt is considered to contain a penta-hypophosphite cation, and corresponds with the formula $[Fe_3(H_2PO_2)_5(OH)_3]H_2PO_2$.

The hetero-acid compounds were prepared in a number of ways, by the action of acids on the 3:8 basic ferric hypophosphite or by the action of sodium hypophosphite or hypophosphorous acid on ferric salts. Six compounds with sulphuric acid are described, formed by the action of the acid on the 3:8 basic salt under varying conditions. These are all either acid or neutral compounds, the three simplest having the formulæ

$$[Fe_3(H_2PO_2)_6](H_2PO_2)SO_4,4H_2O,$$
$$[Fe_3(H_2PO_2)_6](H_2PO_2)_2,\tfrac{1}{2}SO_4,4H_2O, \text{ and}$$
$$[Fe_3(H_2PO_2)_6](SO_4H)_3,xH_2O.$$
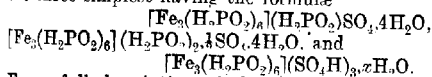
For a full description of the others and of the methods of preparation of all the compounds, the original must be consulted. A nitrate is described, and also an explosive perchlorate, of the formula $[Fe_3(H_2PO_2)_6](ClO_4)_3(H_2PO_2) + \tfrac{1}{2}H_2PO_2 + 18H_2O$. The chlorides and bromides appear to contain complex anions containing iron. Of these, the most interesting is the compound

$$[Fe_3(H_2PO_2)_6][Fe(H_2PO_2)Cl_3],1.H_2PO_2,12H_2O,$$
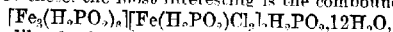
which is readily obtained crystalline in the form of truncated octahedra of fair size by the action of concentrated hydrochloric acid on the 3:8 basic salt.

The compounds are all sparingly soluble in water, by which many of them are slowly hydrolysed, with formation of the 3:6 basic ferric hypophosphite. They are very stable to acids, and there is little tendency for the ferric iron to be reduced by the hypophos-

phorous acid—a further proof that a complex cation is present. Alkalis, alkali carbonates, and ammonium sulphide decompose them, with formation of ferric hydroxide. Their water of crystallisation is very loosely held, and is often lost on exposure to air.

E. H. R.

Crystalline Substances with Colloidal Properties. Basic Zirconium Sulphates and the Molecular State of Zirconium Sulphate in Aqueous Solution. O. HAUSER and H. HERZFELD (*Zeitsch. anorg. Chem.*, 1919, **106**, 1—8).—In aqueous solution, zirconium sulphate is generally supposed to be hydrolysed, with formation of zirconyl sulphates containing the complex anions $ZrO(SO_4)_2''$ and $Zr_2O_3(SO_4)_2''$. This view was supported by the existence of a potassium zirconyl sulphate supposed to have the composition $Zr_2O_3(SO_4)_2K_2$. It is now shown, however, that this formula does not correctly represent the composition of the potassium salt. In reality, the basic compounds formed by the hydrolysis of zirconium sulphate in aqueous solution are much more complex than has been supposed, and three such basic sulphates have now been isolated in crystalline form. Although these compounds are definitely crystalline, yet in solution their properties are essentially colloidal.

(1) The compound $\{Zr_4(SO_4)_3(OH)_{10}\}10H_2O$ appears to exist in two forms. One of these has been previously described (A., 1905, ii, 531). The other is prepared by dissolving zirconium sulphate tetrahydrate in cold water and keeping the 2% solution for several days, when the salt is deposited in the form of needles differing only from the crystals of the first form in their optical properties. The first form is not decomposed by boiling water, whilst the second loses part of its sulphuric acid.

(2) The more basic salt, $\{Zr_5(SO_4)_5(OH)_{22}\}8H_2O$, is prepared by dissolving anhydrous zirconium sulphate in five times its weight of water and precipitating with alcohol. The precipitate is then dissolved in a little warm water and dialysed, and in the course of a few days the basic salt separates in the form of very characteristic spherical crystals which do not lose their shape when dehydrated.

(3) The salt, $\{Zr_7(SO_4)_6(OH)_8\}H_4,4H_2O$, has been previously described (A., 1907, ii, 626), being there given the formula

$$2ZrO_2,3SO_3,5H_2O.$$

The new formula takes account of its acid properties and explains its ready conversion into either of the salts (1) and (2). It parts with its water very reluctantly, only four molecules being lost at 225°.

A potassium zirconyl sulphate of definite composition has been prepared by adding, drop by drop, a saturated solution of potassium sulphate to a strong solution of zirconium sulphate tetrahydrate acidified with sulphuric acid. It has the formula

$$\{Zr_4(SO_4)_5(OH)_8\}K_2.$$
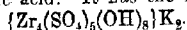
The corresponding zirconyl sulphuric acid could not be isolated.

E. H. R.

Zirconium Alkali Sulphates. ARTHUR ROSENHEIM and JACOB PINSKER (*Zeitsch. anorg. Chem.*, 1919, 106, 9—14).—Hauser and Herzfeld have shown (preceding abstract) that the crystalline basic zirconium sulphates are semi-colloidal in character, and that their composition is influenced to an unusual degree by the temperature and concentration of the solution in which they are formed. It has now been found that the composition of the double salts formed by zirconium sulphate with sulphates of the alkali metals similarly depends on concentration and other conditions. Two such compounds with ammonium sulphate have been prepared, and are now described. When to a solution of 10 grams of anhydrous zirconium sulphate in 20 c.c. of water is added a solution of 14 grams of ammonium sulphate in 25 c.c. of water and the mixture is allowed to evaporate over sulphuric acid, a double salt separates as a crystalline crust. This salt has the composition

$$[(NH_4)_4\{Zr_4(OH)_8(SO_4)_8\}],4H_2O,$$
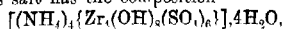
and is evidently the ammonium salt of the zirconyl sulphuric acid described by Hauser (preceding abstract [3]) Subsequently, from the same solution separates a second salt, less basic than the first, and having the composition $(NH_4)_4\{Zr(SO_4)_4\}5H_2O.$ This second salt is apparently only deposited when the acidity of the solution has been sufficiently increased by the separation of the first more basic salt. The second salt dissolves readily in boiling water, and, on cooling, the solution deposits crystals of the first salt.

The double potassium zirconium sulphate, $K_4Zr(SO_4)_4,3H_2O$, prepared by mixing strong solutions of zirconium sulphate and potassium hydrogen sulphate (Rosenheim and Frank, A., 1905, ii, 256), is now found to have a very variable content of water of crystallisation. When normal potassium sulphate is used, a more basic salt is obtained having the composition $K_4\{Zr_4(OH)_8(SO_4)_5\}8H_2O.$ As in the case of the ammonium salts, the product separating from a weakly acid solution is more basic than that from a strongly acid solution. The normal double sulphate, $K_4\{Zr(SO_4)_4\}$ aq., is readily hydrolysed by water at 30°. with formation of complex basic salts, but no product of definite composition could be isolated. On account of their great solubility, basic sodium zirconium sulphates could not be isolated.

All the double salts described have, like the basic zirconium sulphates, colloidal properties. From their heated aqueous solutions. gels are precipitated by electrolytes and by dilute acids. These gels probably consist of colloidal zirconium hydroxide, and only dissolve slowly in excess of strong acid.   E. H. R.

The Nature of Subsidiary Valencies. XXI. Gold Compounds. Ammines of Double Salts. Thermal Decomposition of Double Haloids. FRITZ EPHRAIM (*Ber.*, 1919, 52, [B], 241—254).—The dark brown auric bromide, $AuBr_3$, which is obtained by dissolving precipitated gold in bromine, becomes brownish-yellow in an atmosphere of ammonia, and absorbs about 9 molecules of the gas at the ordinary temperature and about

23 molecules in a freezing mixture. Cæsium auribromide resembles auric bromide very closely in its behaviour towards ammonia, and the pale yellow potassium aurichloride also forms at $-18°$ a dark orange-red compound with about $12NH_3$, which effervesces in water with the evolution of free nitrogen.

Auric bromide has the dissociation temperature, in an atmosphere of bromine, $181°$, the product being aurous bromide, which is yellow at the temperature of boiling naphthalene, but becomes darker when removed from the bath. It forms a diammine (Meyer, A., 1906, ii, 664). The vapour pressure of auric chloride reaches 760 mm. at $256·5°$, but if the salt is left under about 100 mm. pressure at $225°$ until it acquires a pale yellow colour, that is, until it is changed into aurous chloride, and is then heated further in the atmosphere of chlorine, atmospheric pressure is again reached at $289·5°$. That is to say, aurous chloride is only stable in an atmosphere of chlorine over a range of $33°$. Aurous chloride diammine has the dissociation temperature $113·5°$.

Potassium aurichloride melts at the temperature of boiling mercury, but cæsium aurichloride has a slightly higher m. p. At $440°$, however, both salts have vapour pressures of about 350 mm.

The fact that aurichlorides and auribromides of the alkali metals behave towards ammonia exactly like the auric salts suggests that they are dissociated by ammonia into the component haloids. The question is therefore raised whether any double salts do, as such, form ammines, their tendency in this direction being in great contrast to their affinity for water.   J. C. W.

The Attack of Platinum and Gold by the Alkali Hydroxides. L. Quennessen (*Bull. Soc. chim.*, 1919, [iv], 25, 237—240).—A discussion of the results of Nicolardot and Chatelot (compare this vol., ii, 161), and of results published in *Bull. Usines guerre*, 1918, No. 17, 134, from which the author concludes that pure platinum shows the highest resistance to acid reagents, and that, whilst certain alloys of gold and palladium show a high resistance to the action of alkali hydroxides, silver vessels are the more convenient for laboratory purposes.   W. G.

A New Method of Preparation of certain complex Compounds of Platinum and of its Analogues. L. Tschugaev (*Bull. Soc. chim.*, 1919, [iv], 25, 234—237).—Potassium platinonitrite reacts with ammonia in the cold to give *cis*-dinitrodiamminoplatinum (compare Tschugaev and Kiltinovic, T., 1916, 109, 1286). The similar iodo-*compound*, $Pt,2NH_3,I_2$, may be obtained by boiling potassium platinoiodide in aqueous solution with ammonia. If the ammonia is replaced by methylamine, *di-iododimethylaminoplatinum*, $PtI_2,2NH_2Me$, is obtained.

The same method may be used for preparing certain complex compounds of rhodium. Thus, if rhodium iodide is warmed in aqueous solution with an excess of ammonia, the *compound*, $RhI_3,3NH_3$, reddish-brown, microscopic prisms, is obtained.   W. G.

Recovery of Platinum and Alcohol from Potassium Estimations. A. E. SMOLL (*J. Ind. Eng. Chem.*, 1919, 11, 466—467).—The alcoholic filtrates and washings are distilled until all alcohol has been removed; platinum black and water remain in the distillation flask. The distillate is then heated under a reflux apparatus through which a current of warm water is passed so that the temperature of the escaping water is 58°. The top of the reflux apparatus is connected with a condenser, and the heating is continued until all aldehyde has been expelled, as is ascertained by testing drops of the distillate. The alcohol is finally fractionated from a small quantity of sodium hydroxide. [See, further, *J. Soc. Chem. Ind.*, 1919, 444A.] W. P. S.

Solubility of Hydrogen in Palladium Mixed Crystals. G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1918, 72—78; from *Chem. Zentr.*, 1919, i, 338).—A definite limit for the solubility of hydrogen in palladium, analogous to the limits of action of other agents on mixed crystals of gold with silver or copper (A., 1918, ii, 445, 447), is shown to exist at that region of temperature in which a change of position of the two types of atom in the palladium mixed crystal is no longer perceptible. The limit lies at ⅓ mol. Pd. Taking into account the atomic structure of the palladium mixed crystal, it appears, therefore, that the hydrogen atom can only enter and continue to oscillate at lattice axes which are parallel to the diagonals of the cube which are mainly occupied by palladium atoms. H. W.

Mineralogical Chemistry.

A Chemical Investigation of Banded Bituminous Coal. Studies in the Composition of Coal. FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER (T., 1919, 115, 619—636).

"Blue John" and other Forms of Fluorite. BERTRAM BLOUNT and JAMES HARRY SEQUEIRA (T., 1919, 115, 705—709).

Chubutite, a New Lead Mineral. HÉRCULES CORTI (*Anal. Soc. Quím. Argentina*, 1918, 6, 65—72).—The mineral to which the name *chubutite* is given occurs in the Gobernación del Chubut (Argentine) in radiated masses of obscure, crystalline structure. D 7·95, hardness 2·5, of a yellow colour and easily reduced to powder. Analysis gave:

Al₂O₃	Fe₂O₃	PbO	PbCl₂	Sb₂O₃	As₂O₃	Insol.	Total.
0·12	0·19	83·30	14·83	0·69	trace	0·76	99·89

This leads to the the formula 7PbO,PbCl₂. The crystalline structure appears to be tetragonal. W. S. M.

A Titaniferous Mineral from the Sierra del Pié de Palo, San Juan (Argentine). 'LUCIANO R. CATALANO (*Anal. Soc. Quím. Argentina*, 1918, **6**, 35—48 and 83—93).—A detailed account of the chemical analysis of the mineral in question. The formula FeTiO₃,MnTiO₃ is established. The mineral corresponds in composition with kibdelophane, a variety of ilmenite.   W. S. M.

Analytical Chemistry.

Colorimetric Determination of the Hydrogen-Ion Concentration in Small Quantities of Solution. A. R. C. HAAS (*J. Biol. Chem.*, 1919, **38**, 49—55).—The preparation of indicator papers which may be used for the rapid estimation of hydrogen-ion concentration is described. The method yields accurate results, and is of considerable value when it is impossible to carry out the electrometric method.   J. C. D.

Accuracy of Different Methods of Measuring Small Volumes of Fluid. FREDERICK WILLIAM ANDREWES (*Biochem. J.*, 1919, **13**, 37—44).—A study of the inaccuracies attendant on the methods employed for measurement of small volumes and dilutions, such as are used in serological investigations.   J. C. D.

Preparation of Stable Starch and Oxalic Acid Solutions by means of Metallic Mercury. A. JUNK (*Chem. Zeit.*, 1919, **43**, 258).—The solution is treated with a few c.c. of mercury, boiled, and shaken, so that the mercury is finely subdivided; the mercury is allowed to remain in the bottle containing the solution. Such treatment prevents the growth of moulds, etc., in the solutions, and the latter may be kept for years without altering in strength, even when the bottle is opened frequently.   W. P. S.

Identification of Iodine in Blood by a Microcrystal-lographic Method. ULRICH HINTZELMANN (*Zeitsch. physiol. Chem.*, 1919, **104**, 211—216).—The method proposed by Karfunkel (*Deut. med. Woch.*, 1912, 643), which depends on the isolation of crystals of iodohæmatin, is untrustworthy for ordinary use.
    J. C. D.

Modification in the Technique of Fischer's Reaction for Hydrogen Sulphide. LUCIANO P. J. PALET and AMANCIO FERNANDEZ (*Anal. Soc. Quím. Argentina*, 1918, **6**, 49—51).—On account of the inconvenience in preparing and keeping *p*-amino-dimethylaniline sulphate, the following procedure is substituted.

To a drop of dimethylaniline are added 2 c.c. of water, three to four drops of a 1% solution of sodium nitrite, and five drops of 10% hydrochloric acid. The liquid is neutralised with saturated sodium carbonate solution, and the nitroso-base extracted with ether. To the ethereal solution, zinc powder and a few drops of concentrated hydrochloric acid are added. When the reduction is complete, the ether layer is decanted off, 2 c.c. of water and the solution to be tested are added, then concentrated hydrochloric acid, and a few drops of 10% ferric chloride solution. The addition of a little alcohol renders the appearance of the resulting methylene-blue more distinct. It is necessary that hydrochloric acid be present in great excess. W. S. M.

Estimation of Sulphuric Acid and Sulphates. G. MEILLÈRE (*J. Pharm. Chim.*, 1919, [vii], 19, 296—297).—In the estimation of sulphates by precipitation as barium sulphate, the precipitate should be collected while the solution is still hot and washed with hot dilute acetic acid solution. In the case of sulphuric acid, this may be neutralised with barium hydroxide solution, using phenolphthalein as indicator, and a very slight excess of the barium hydroxide then added; the mixture is acidified with acetic acid, kept at 100° for two hours, and the precipitated barium sulphate then collected. [See, further, *J. Soc. Chem. Ind.*, 1919, July.]
W. P. S.

Method for the Volumetric Estimation of Sulphates. A. C. D. RIVETT (*Chem. News*, 1919, 118, 253—254).—The method is intended primarily for works purposes, and depends on double decomposition between moist, precipitated barium oxalate and certain dissolved sulphates, whereby soluble oxalates are produced which may be titrated with potassium permanganate. [For details, see *J. Soc. Chem. Ind.*, 1919, 481A.] W. E. F. P.

Continuous Process for the Estimation of Nitrogen by Dumas's Method. LUDWIG DEXHEIMER (*Zeitsch. anal. Chem.*, 1919, 58, 13—19).—To avoid the necessity of cooling the combustion tube after the completion of one estimation and before another can be started, a procedure is described for removing and inserting successive boats while the tube is still hot. The essential feature consists of means for passing the current of carbon dioxide in a reverse direction through the tube while the latter is opened at one end. Provision is also made for oxidising the reduced copper when necessary. W. P. S.

The Estimation of Total Nitrogen in Soils containing Rather Large Amounts of Nitrates. R. S. SNYDER (*Soil Sci.*, 1918, 6, 487—490).—If the organic matter of the soil is within the usual average (0·8—3·0%), the Hibbard or the "mercury" methods of carrying out the Kjeldahl digestion give quite accurate

results for total nitrogen, even if 10% of the nitrogen is present as nitrate. Methods for total nitrogen, modified to include nitrate nitrogen, such as Ulsch's method, must, however, be used if the organic carbon content of the soil is lower than 0·5%.   W. G.

Estimation of Nitrite and Nitrate Nitrogen in the Presence of other Nitrogen Compounds. Th. Pfeiffer and W. Simmermacher (*Landw. Versuchsstat.*, 1919, **93**, 65—76).— For the estimation of the various forms of nitrogen in such substances as soil extracts, the total nitrogen other than nitric nitrogen is estimated by Kjeldahl's method, using 5 grams of ferrous sulphate. Ammonia nitrogen is estimated by distillation with magnesium oxide; after the ammonia has been removed, the residual solution is treated with 12 grams of magnesium chloride and 3 grams of finely divided copper–magnesium alloy (compare A., 1917, ii, 504), and again distilled to obtain the ammonia derived from the nitrites and nitrates. To estimate the nitrate nitrogen, 75 c.c. of the extract are boiled for one hour with the addition of 1·5 grams of dextrose, 0·3 gram of ferrous sulphate, and 5 grams of sodium carbonate; ammonia and nitrite nitrogen are thus expelled, and the solution is then distilled with copper–magnesium alloy as described. [See, further, *J. Soc. Chem. Ind.*, 1919, July.]
   W. P. S.

Scrubber for Ammonia Distillations. B. S. Davisson (*J. Ind. Eng. Chem.*, 1919, **11**, 465—466).—The scrubber or still-head described consists of a bulb of about 200 c.c. capacity provided with an exit tube at the top, through which the steam, etc., passes to the condenser, and a lower tube or stem for connecting the bulb to the distillation flask. This lower tube extends into the bulb, and is then bent downwards to nearly the wall of the bulb; the tube ends in a small bulb having three openings in the same horizontal plane. The first portion of steam which enters the bulb condenses, and the water flows down about the small bulb, there acting as a scrubbing solution for the remainder of the vapours.   W. P. S.

Albuminoid Ammonia Test. Evelyn Ashley Cooper and Joseph Alan Heward (*Biochem. J.*, 1919, **13**, 25—27).— Potassium permanganate may contain a stable nitrogenous impurity which cannot, as a rule, be removed by prolonged boiling with alkali. This impurity yields ammonia, particularly when the permanganate–alkali mixture is boiled in the dilute condition, and the error involved may be so great as to vitiate the value of the albuminoid ammonia test altogether. [See, further, *J. Soc. Chem. Ind.*, 1919, 438a.]   J. C. D.

Identification of Arsenious Acid. Reply to Tunmann. R. Wasicky and A. Mayrhofer (*Pharm. Post.*, 1918, **51**, 409—410; from *Chem. Zentr.*, 1919, ii. 224).—The authors do not agree with Tunmann's observations (A., 1918, ii, 453) on the

extension of microchemical methods to the detection of arsenic in pharmaceutical preparations, and, further, point out that the destruction of organic matter by concentrated sulphuric acid on the object-glass does not suffice for the detection of arsenic in all possible forms of combination.　　　　　　　　　　H. W.

Estimation of Boric Acid. PAUL JANNASCH and FRIEDRICH NOLL (*J. pr. Chem.*, 1919, [ii], .99, 1—33).—Alcoholic sodium ethoxide solution is recommended for the titration of boric acid solutions in the presence of glycerol; the interfering action of carbon dioxide is thus eliminated. For the estimation of boric acid in minerals, the sample is fused with sodium phosphate and metaphosphoric acid, the boric acid distilled in the presence of methyl alcohol and phosphoric acid, and titrated after the methyl alcohol has been expelled from the filtrate. [See, further, *J. Soc. Chem. Ind.*, 1919, 411A.]　　　　　　　　　　W. P. S.

Estimation of Free Carbon Dioxide in Water. HARTWIG KLUT (*Ber. deut. pharm. Ges.*, 1919, 29, 344—359).—Directions are given for the estimation of free carbon dioxide in water at the source of the latter. The titration is made with sodium carbonate solution, phenolphthalein is used as the indicator, and potassium sodium tartrate is added to the water to prevent interference by ferrous salts.　　　　　　　　　　W. P. S.

Estimation of Free Carbon Dioxide in Water. RUDOLF CZENSNY (*Zeitsch. anal. Chem.*, 1919, 58, 1—12).—To ensure that the correct quantity of indicator is present, a combined solution containing 2·6525 grams of sodium carbonate and 2·5 grams of phenolphthalein is used for the titration of the free carbon dioxide. One hundred c.c. of the water are titrated with this solution; the number of c.c. used, less 0·52 c.c., is multiplied by 1·22 to obtain the mg. of free carbon dioxide per 100 c.c. of water.　　W. P. S.

Micro-elementary Analysis. ERNST MÜLLER and HERTHA WILLENBERG (*J. pr. Chem.*, 1919, [ii], 99, 34—44).—A suitable apparatus is described for the determination of carbon and hydrogen in small quantities (2 to 5 mg.) of substance. The apparatus is constructed entirely of glass, rubber connexions are not used, a single burner is used for heating the combustion tube, and the oxygen is prepared from potassium dichromate and Caro's acid.　　　　　　　　　　W. P. S.

Efficiency of Potash Absorption Apparatus and Comparative Trials with a New Form of Helical Apparatus. J. FRIEDRICHS (*Zeitsch. angew. Chem.*, 1919, 32, 129—132).—A new form of potash absorption apparatus for combustion analysis is described consisting of two cylindrical vessels of light glass fused one inside the other. The gas enters at the top of the inner vessel

and passes through a hole at the bottom into the annular space between the two vessels. A spiral is moulded on the outer wall of the inner vessel so that its apex leaves only a small clearance in the annular space, and the bubbles of gas emerging from the inner vessel are compelled to follow the spiral path in their passage up to the exit, whilst at the same time the displaced liquid is free to circulate through the narrow clearance between the helix and the outer vessel. At the top an exit orifice is provided, on which is fitted, with a ground-in joint, a bent calcium chloride tube. The whole apparatus, when filled, weighs only about 38 grams and contains 10 c.c. of potash solution. It is compact and not liable to breakage, the whole surface can easily be wiped clean, and if the liquid is sucked back there is ample room in the capacious inner vessel to prevent loss. The path travelled by the bubbles of gas is about 25 cm. long, and yet the resistance pressure of the liquid is equivalent to only 5 cm. The efficiency of this apparatus has been tested comparatively with a number of well-known types of other absorption apparatus with different speeds and quantities of carbon dioxide in air, and the results were most favourable.

J. F. B.

Studies of Acidosis. XIII. A Method for Titrating the Bicarbonate Content of the Plasma. DONALD D. VAN SLYKE, EDGAR STILLMAN, and GLENN E. CULLEN (*J. Biol. Chem.*, 1919, **38**, 167—178).—Blood is drawn with precautions against loss or accumulation of carbon dioxide. Two c.c. of the plasma are measured into a round-bottomed flask of 150 to 200 c.c. capacity, and 5 c.c. of $0.02N$-hydrochloric acid are added. Carbon dioxide is removed by vigorous shaking, and titration is carried out with $0.02N$-carbonate-free sodium hydroxide, using neutral-red or phenolsulphonephthalein as indicator until the colour of the solution matches one of known hydrogen-ion concentration. The results agree well with those given by the carbon dioxide capacity method over a range of bicarbonate concentrations ($0.03—0.01M$) ordinarily encountered in man, even in severe acidosis.

J. C. D.

Microchemical Distinction of Sericite and Talc. O. HACKL (*Verh. geol. Reichanst. Wien*, 1918, 1; from *Chem. Zentr.*, 1919, ii, 225—226).—The macrochemical distinction of sericite from talc is tedious, since the former frequently contains magnesium and the latter aluminium. The following microchemical method is proposed. A small quantity of the finely powdered specimen is boiled with concentrated hydrochloric acid in a small platinum spoon, the precipitate is allowed to subside, and the supernatant liquid is drawn off with a small pipette and evaporated in a platinum lid to remove the bulk of the acid, which cannot be neutralised, since the process involves the introduction of too large quantities of salt into the solution, whereby further concentration is hindered. The residue is warmed with a small quantity of water containing a trace

of hydrochloric acid; the undissolved matter is allowed to separate, and the clear liquid withdrawn with a capillary pipette. A drop of this solution is tested for potassium with freshly prepared platinic chloride solution, preferably using a cover-glass of quartz; a second drop is tested for aluminium by addition of cæsium chloride in the presence of sodium sulphate, which renders possible the formation of the alum. Magnesium is detected by the usual method in a third drop after precipitation of any considerable amount of aluminium by addition of ammonia; the precipitate need not be removed. H. W.

Estimation of Mercury in Mercury Salicylate. A. OSTANTINO (*Giorn. Farm. Chim.*, 1918, 67, 7—12; from *Chem. entr.*, 1919, ii, 4—5).—Mercury salicylate (0·25 gram) is warmed 1 a porcelain dish on the water-bath for about six minutes with ncentrated sulphuric acid (2 c.c.). The solution is diluted with ater to 160 c.c. and electrolysed in a platinum dish during four- en minutes, a rotating platinum anode and a current of 6 amperes t 5 volts being used; without interrupting the current, the deposit ; washed successively with water, alcohol, and ether, and dried in desiccator. A mercury cathode may be used in place of a latinum dish, in which case the volume of the solution should not e more than 30 c.c., and the current 3 amperes at 7—10 volts. he process is more advantageous than those previously described nd more convenient than those of the United States Pharma- opœia, 1916. H. W.

The Conductivity as Indicator in Titrations with Potassium Permanganate. VICENTE VILLUMBRALES (*Anal. Fis. Quim.*, 1919, 17, 100—114).—In the titration of ferrous salts y means of permanganate solution, free acid is consumed according to the equation $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + MnSO_4 + 8H_2O$. Ordinarily, acid is added in great excess to dissolve the colloidal manganese oxide formed, and the conductivity of the mixture during the titration remains prac- tically constant. In presence of insufficient acid, the conductivity falls with the addition of the permanganate solution until the oxidation is complete, and thereafter remains constant, the end- point being indicated by a sharp angle in the curve. In the oxidation of manganous salts in neutral solution by means of per- manganate, acid is formed: $3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4$. In this case, the conductivity increases during the titration, and becomes constant on completion of the oxidation. W. S. M.

Use of Colloidal Silica in Iron Titrations. E. DITTLER *Chem. Zeit.*, 1919, 43, 262).—The author confirms the statement y Schwarz and Rolfes (this vol., ii, 170) that colloidal silica, in he presence of manganous salts, prevents the oxidation of hydrogen hloride. [See, further, *J. Soc. Chem. Ind.*, 1919, July.]
W. P. S.

Iodometric Estimation of Chromic Acid. I. M. KOLTHOFF and E. H. VOGELENZANG (*Pharm. Weekblad*, 1919, **66**, 514—524). —In the presence of sufficient acid (at least 20 c.c. 4N-hydrochloric acid in 100 c.c. of solution), the mixture may be titrated immediately after the addition of the reagents, even in the case of dilute chromate solutions. If insufficient acid is present, too much thiosulphate is consumed, owing to the occurrence of a side-reaction, the nature of which is not clearly ascertained, although it is shown that a possible oxidation of the hydriodic acid formed by air is not involved. The side-reaction is accelerated by sunlight, especially in presence of ammonium molybdate. Ammonium molybdate, on the other hand, retards the reaction between chromic acid and hydriodic acid. In strongly acid solutions, ferrous salts have a negative catalytic effect; in very weakly acid solutions, the effect is positive.   W. S. M.

Analysis of Zirconium Minerals and Alloys. A. TRAVERS (*Chim. et Ind.*, 1919, **2**, 385—392).—The mineral is fused with sodium peroxide, cooled, and extracted with water; zirconium oxide, titanium oxide, ferric oxide, manganese oxide, rare earths, and a portion of the silica remain insoluble, whilst silica (remainder), aluminium, and phosphoric acid pass into solution. The insoluble portion is dissolved in hydrochloric acid and treated, after neutralisation, with sodium thiosulphate; the precipitate is collected, ignited, and weighed, and allowance made for the amount of silica and titanium oxide contained in it. The former is estimated by treatment with hydrofluoric acid and the latter colorimetrically after fusion with potassium hydrogen sulphate. The iron is estimated by titration with titanium trichloride solution, manganese by the persulphate method, and rare earths by precipitation with oxalic acid. Aluminium may be estimated in zirconium–iron alloys by precipitating the zirconium and aluminium together by treatment with sodium thiosulphate after the greater part of the iron has been removed by extraction with ether, and then separating the aluminium by fusion with an alkali. [See, further, *J. Soc. Chem. Ind.*, 1919, 421A.]   W. P. S.

Electro-analysis of Gold without Platinum Electrodes. J. GUZMÁN (*Anal. Fis. Quim.*, 1919, **17**, 115—120).—Preliminary analyses were carried out with an iron anode and a cathode of platinum gauze. The electrolyte was prepared by dissolving about 0·1 gram of gold in aqua regia, adding 3 grams of sodium hydroxide in 20 c.c. of water, and then 10 c.c. of freshly prepared 2% potassium cyanide solution. The electrolysis was carried out with the temperature rising to 60°, with rapid agitation of the electrolyte. Voltage, 1·9. The results obtained were excellent. A slight disintegration of the iron anode observed in this procedure was avoided by evaporation of the solution of the gold in aqua regia to remove the nitric acid. The gold was removed from the cathode by electrolysis in hydrochloric acid. Analyses with a

cathode of gilded copper gauze gave defective results. Excellent results were, however, obtained with the use of a cathode of very fine copper gauze previously nickel-plated. If the gold contains copper, it was found necessary to add 1 gram of potassium cyanide more than is required for the solution of the precipitate, and to keep the voltage below 1·9. The deposit was washed first with a dilute (2%) solution of sodium sulphite, then with water, and finally with alcohol.

<div align="right">W. S. M.</div>

Determination of the Methane Content of Mine Gases or of the Concentration of a Gas in a Gaseous Mixture. FRIEDRICH KRÜGER, OTTÓ REINKOBER, and HANS RIEGGER (D.R.-P. 309627; from *Chem. Zentr.*, 1919, ii, 39—40).—The process depends on the property of methane of absorbing ultra-red rays. The diminution in intensity of a beam of rays caused by absorption is measured in the usual manner by means of thermocouples, bolo-meter, or selenium cells. The process is also applicable to other technical mixtures of gases.

<div align="right">H. W.</div>

The Isolation and Characterisation of Alcohols as Allophanates. A. BÉHAL (*Compt. rend.*, 1919, **168**, 945—947).— The method of preparation of the allophanates consists in passing a current of cyanic acid gas into the alcohol, filtering off the pro-duct, washing it with ether, and recrystallising the allophanate from absolute alcohol, benzene, or acetone. The alcohol is charac-terised by the m. p. of its allophanate, and then the alcohol is regenerated and its physical constants determined. This method can be applied to tertiary alcohols. The terpenic alcohols, except linalool, behave normally in this method, as do also the cyclic alcohols, except terpineol, unless a phenolic group is present. If the phenolic group is converted into an alkyloxy- or aryloxy-group, the reaction then proceeds normally. Alcohols having an ethenoid linking, either in the cyclic or acyclic series, give normal allo-phanates.

<div align="right">W. G.</div>

Optical Activity and Quantitative Estimation of Menthol Dissolved in Eugenol and Phenol. OSCAR VON FRIEDRICHS (*Arch. Pharm.*, 1919, **257**, 72—78).—Mixtures of menthol, eugenol, and phenol are used as local anæsthetics, particularly in dentistry, and a solution of menthol (40%), phenol (40%), and eugenol (20%) is described in the latest addition of the Swedish Pharmacopœia under the name "tinctura antiodontalgica." For the estimation of the menthol content, the author has determined the specific rotation, at 18°, of solutions of menthol in phenol ($p=25$—50), in eugenol ($p=10$—50), and in mixtures of phenol and eugenol (2:1, 1:1, 1:2), and has derived formulæ by which the menthol content may be directly calculated from the optical activity.

<div align="right">H. W.</div>

Use of Methylene-blue for the Detection of Sugar in Urine. LIEBERS (*Deutsch. med. Woch.*, 1916, **42**, 1197; from *Bied. Zentr.*, 1919, **48**, 81).—Six drops of the urine are treated

with 5 c.c. of 0·1% methylene-blue solution and ten to twenty drops of potassium hydroxide solution, and the mixture is boiled; if sugar is present in the urine, the blue colour fades, the rate at which it disappears depending on the amount of sugar. Other reducing substances in the urine do not interfere with the test.

W. P. S.

Estimation of Blood Sugar by the Modified Picric Acid Method. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1919, **37**, 503—504).—It is pointed out that the final acidity of the sodium picrate-picric acid solution used for removal of the blood proteins should be about 0·05—0·04N. If this is not ensured, the reagent may fail to precipitate the proteins satisfactorily (compare Rohde and Sweeney, this vol., ii, 84).   J. C. D.

Estimation of Reducing Sugars Volumetrically by Schindler's Modification of Bertrand's Method. BETTINGER (*Bull. Assoc. Chim. Sucr.*, 1918, **35**, 111—113).—Bertrand's volumetric method of determining reducing sugars (A., 1907, ii, 136), in which the precipitated cuprous oxide is dissolved in ferric sulphate solution and the liquid titrated with permanganate, has been rendered more rapid by using the same flask throughout and by replacing the filter-tube by a Gooch crucible. Reduction is effected in a conical flask, and the cuprous oxide washed quickly by decantation through a Gooch crucible provided with an asbestos pad, taking care to carry over as little of the precipitate as possible. Ferric sulphate solution of known titre is added to the precipitate remaining in the reduction flask, which is immediately connected by means of a rubber stopper and funnel with the Gooch crucible, and also with a tube leading to a filter-pump. A further known volume of the ferric sulphate solution is added to the Gooch crucible to dissolve the cuprous oxide remaining on the asbestos pad, and the liquid is drawn into the flask. After washing with warm water, the solution in the reduction flask is titrated with permanganate.   J. P. O.

Behaviour of Inulin in the Animal Body. Application of the Benedict Method to the Estimation of Lævulose and Inulin. RUTH E. OKEY (*J. Biol. Chem.*, 1919, **38**, 33—42).— Benedict's method for the estimation of dextrose (A., 1918, ii, 247) may be applied with success to the estimation of lævulose and of inulin. It is necessary in some cases to eliminate the disturbing influence of certain salts.   J. C. D.

Estimation of Furfuroids (Furfurosans) in the Different Products of Beet-sugar Factories. II. R. GILLET (*Bull. Assoc. Chim. Sucr.*, 1918, **35**, 93—102).—In a previous paper (A., 1918, ii, 248), it was shown that in the determination of pectic substances in beet-sugar factory products by the Tollens-Councler

procedure, sucrose and hexoses in general yield a certain amount of furfuraldehyde, the quantity of which, in spite of precautions to ensure uniformity, is variable. Satisfactory results, however, are claimed to have been obtained by a preliminary elimination of the hexose sugars by fermentation, after which the liquid is distilled with hydrochloric acid and the phloroglucide precipitated and weighed in the usual manner. Operating in this way, the amount of pentosans and "pectic substances" in beet molasses, per cent. of the non-sugars present, was found to average 2·10 and 5·70 respectively. In the case of first- and second-grade sugars, the proportions were considerably higher, from which the author concludes that a large part of the so-called furfurosans or furfuraldehyde-yielding substances present in the clarified syrups are retained by the sugars when drying in the centrifugals.

J. P. O.

Filter for Use in the Estimation of Crude Fibre, etc. F. MACH and P. LEDERLE (*Chem. Zeit.*, 1919, **43**, 251).—A disk of fine platinum gauze (16 to 17 meshes per cm., each mesh 0·5 mm. wide) is placed on a perforated porcelain plate contained in a funnel, and asbestos fibre or pulp is introduced so as to form a layer on the gauze.   W. P. S.

Systematic Extractions with Ether. JOH. PINNOW (*Zeitsch. Nahr. Genussm.*, 1919, **37**, 49—65).—At 15°, the distribution coefficient of glycollic acid between water and ether is 32, and of formic acid 2·4; at 26°, the coefficients are 38 and 2·5 respectively. The extraction of succinic acid, oxalic acid, malic acid, etc., from half-saturated solutions has been investigated. Lactic acid and citric acid may be separated and identified by extraction and use of the distribution coefficients. A substance which is not readily extracted may be estimated by making a series of successive and similar extractions; complete extraction is unnecessary.

W. P. S.

New Process for the Estimation of Oxalic Acid. ERWIN OTT (*Ber.*, 1919, **52**, [*B*], 752—753. Compare H. Krause, this vol., ii, 203).—The quantitative decomposition of oxalic acid into carbon monoxide, carbon dioxide, and water by acetic anhydride in the presence of a trace of sulphuric acid had previously been described by the author (A., 1913, i, 1302), and had been attributed by him to the intermediate formation of oxalic anhydride; it had not, however, been adapted by him to the rapid and exact estimation of oxalic acid and its salts.   H. W.

Recovery of Ether in Fat Estimations. J. GROSSFELD (*Zeitsch. Nahr. Genussm.*, 1919, **37**, 81—82).—A considerable portion of the ether used in fat extractions remains in the extraction thimble; this portion of the solvent may be recovered if, as

soon as the extraction is completed, the thimble and its contents are transferred to a suitable apparatus and distilled   W. P. S.

Detection of Acetone in Urine. OTTO MAYER (*Zeitsch. physiol. Chem.*, 1919, **104**, 220—228).—A general review of the methods for detecting and estimating acetone in urine. A modification of the Legal test is described which gives a reaction with acetone present in a dilution of 1:1000.   J. C. D.

Nephelometric Estimation of Acetone in Urine. G. ISSOGLIO (*Giorn. Farm. Chim.*, 1917, **66**, 301—303; from *Chem. Zentr.*, 1919, ii, 150).—For the estimation of small quantities of acetone. the turbidity due to iodoform, and obtained by the use of alkaline iodine–potassium iodide solution, is compared with that given by a similarly treated solution of acetone (0·01%). The tests are performed in two similar crystallising dishes 7 cm. in diameter and 4 cm. high. Urine (100 c.c.) is mixed with half its volume of water. and 100 c.c. of the distillate are collected. The distillate (10 c.c.) is mixed with sodium hydroxide solution (5%, 10 c.c.) and water (30 c.c), and iodine–potassium iodide solution (5%, 10% KI, 5 c.c.) is added. The turbidity obtained is compared with that simultaneously given by 10 c.c. of acetone solution (0·01%). If the acetone content of the distillate is greater than that of the control, a proportionately smaller volume is taken. which is then diluted to 10 c.c.; in the reverse case, less of the control solution is taken, but the volume of the samples must invariably be made up to 10 c.c.. so that the volume of solution in the dish always amounts to 50 c.c. It is observed that the rapidity with which the turbidity appears is, within certain limits, proportional to the acetone content.   H. W.

Estimation of Urea in Urine by Direct Nesslerisation. OTTO FOLIN and GUY E. YOUNGBURG (*J. Biol. Chem.*, 1919, **38**, 111--112).—The preparation of a urease product is described, the use of which permits urea nitrogen to be determined directly by Nesslerisation.   J. C. D.

Rapid Method for the Estimation of Urea in Urine. JAMES B. SUMNER [with AARON BODANSKY] (*J. Biol. Chem.*, 1919, **38**, 57—61).—To 1 c.c. of urine in a centrifuge tube is added 1 c.c. of a phosphate solution and urease. The reaction is assisted by maintaining the tube warm for twenty minutes. The proteins are then removed by potassium mercury iodide and centrifugalisation, and the ammonia estimated in an aliquot part of the supernatant fluid. The method gives results which agree well with those carried out by the aeration method.   J. C. D.

Estimation of Urea and Non-Protein Nitrogen in Blood and Tissue by Means of Nessler Reagent. A. GRIGAUT and FR. GUÉRIN (*J. Pharm. Chim.*, 1919, [vii], **19**, 233—243, 281—294).—From 1 to 3 c.c. of blood, serum, etc., is mixed with

2 to 6 c.c. of a suspension of 1 gram of soya-bean flour in 100 c.c. of water containing 0·4 gram of sodium dihydrogen phosphate; the mixture is kept at 56° for fifteen minutes, then treated with its own volume of 20% trichloroacetic acid, filtered, and the ammonia is estimated in the neutralised filtrate by means of Nessler reagent; the quantity of ammonia found is a measure of the urea present. To estimate non-protein nitrogen, the substance (blood, tissue, etc.) is thoroughly macerated and extracted with chloroform water, the extracts are treated with trichloroacetic acid to precipitate proteins, and, after filtration, a portion of the filtrate is digested with a mixture of phosphoric acid, three parts, and sulphuric acid, one part, and containing one-fifteenth of its volume of 10% copper sulphate solution. The ammonia formed is then estimated directly in the neutralised solution by means of Nessler reagent.   W. P. S.

Analysis of Mercury Fulminate. A. LANGHANS (*Zeitsch. anal. Chem.*, 1918, **57**, 401—445).—A method described for the estimation of mercury fulminate depends on the formation of hydroxylamine when the fulminate is dissolved in 12% hydrochloric acid; the hydroxylamine is estimated by boiling the hydrochloric acid solution with the addition of iron alum solution, and then titrating the hot mixture with $N/20$-permanganate solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 389A.]   W. P. S.

Tungstic and Molybdic Complexes as Precipitants of Organic Bases. LUIS GUGLIALMELLI (*Anal. Soc. Quim. Argentina*, 1918, **6**, 57—64).—Solutions of the sodium salts of the following acids in dilute hydrochloric acid were prepared: tungstic, arsenotungstic, silicotungstic, phosphotungstic. molybdic, arsenomolybdic, hosphomolybdic, arsenotungstomolybdic. arsenovanadotungstic. The effects of these reagents on the following organic bases in ilute hydrochloric acid solution were observed and tabulated: - and β-naphthylamine, benzidine, antipyrine, pyramidone, affeine, pyridine, nicotine, quinoline, cinchonine, cocaine, uramine.   W. S. M.

A Reaction of Aconitine. L. P. J. PALET (*J. Pharm. Chim.*, 919, [vii], **19**, 295—296).—Crystallised aconitine yields a violet oloration when heated with phosphoric acid solution (D 1·7); morphous aconitine gives a grey coloration with the test. Both orms of aconitine give a violet coloration if the phosphoric acid ꞏ mixed previously with 4% of its weight of sodium molybdate. ᴺspidospermine and veratrine also give a violet coloration under hese conditions, but the former may be identified by the action f oxidising substances on it, and the latter by means of its reaction with mineral acids. Other alkaloids do not give a violet oloration. [See, further, *J. Soc. Chem. Ind.*, 1919, July.]   W. P. S.

Detection of the Poisons which can be Extracted with Ether from the Acid Aqueous Solution in the Stas-Otto Process. III. O. TUNMANN (*Apoth. Zeit.*, 1918, **33**, 443—444, 447—448, 454—455; from *Chem. Zentr.*, 1919, ii, 42—43. Compare A., 1918, ii, 139).—*Colchicine.*—The residue, obtained according to Stas-Otto, is an amorphous, brownish-yellow mass with a very bitter taste. The sublimates are dull white or yellow and amorphous. Hydrochloric and sulphuric acids colour the sublimate yellow. The solution in sulphuric acid becomes pale green, blue, and violet on addition of a little nitric acid. Nitric acid gives a violet, greenish-yellow, and yellow coloration, which becomes red on addition of alkali. Phenol solution causes the separation of minute drops from the aqueous solution of the sublimate. Ferric chloride imparts a dark green or olive-green colour, but only dissolves the sublimate when warmed, the coloration becoming more intense.

Caffeine can be immediately sublimed from all its pharmaceutical preparations, and also from blood or urine; it is more difficult, and often not directly possible, to obtain similar sublimates from theobromine. Caffeine sublimates consist of needles and prisms with direct extinction, and six-sided platelets; theobromine sublimates never exhibit these large crystals, but are composed of needles and masses of small nodules. If the sublimates are moistened with nitric acid (5%) and a drop of silver nitrate solution (5%) is added, large, rounded nodules, from which fine, bent crystal threads project, are observed with caffeine, whilst theobromine yields large sheaves and tufts composed of long, colourless, rectangular rods, which have oblique extinction and polarise strongly in all colours. The reaction with mercuric chloride can also be applied to theobromine; the crystals of theobromine mercuric chloride polarise in colours, generally have oblique extinction, but are composed of small groups which cannot always be recognised even with a lens. Mercuric chloride and gold chloride are not suitable reagents for distinguishing between caffeine and theobromine. With bromine–potassium bromide, crystals differing from those described by Eder (A., 1917, ii, 346) can be obtained if the caffeine sublimate is first dissolved in the bromine–bromide solution and hydrochloric acid is carefully added; in addition to a few needles (10—20 μ), single, yellow crystals separate, round which prisms gradually group themselves. All the crystals are more or less colourless after an hour. Under these conditions, theobromine does not give a precipitate. When caffeine or theobromine sublimates are treated with hydriodic acid and the solutions warmed until gas commences to be evolved, a portion of the bases collects in black lumps, whilst the remainder passes into solution; small, blackish-brown rhombs and four-sided plates separate from the caffeine solution, which appear red between crossed Nicols, show very faint pleochroism, and finally unite to irregular masses. From the theobromine solution, much larger, flat, four-sided or rhombic platelets crystallise, which show unusually marked

pleochroism and, generally, oblique extinction. Caffeine and theo-
bromine are most readily distinguished by means of nitric acid.
If the sublimates are warmed with concentrated nitric acid until
a colourless rim is formed, caffeine nitrate separates in the same
form as by sublimation or can be identified as chloralcaffeine, whilst
the theobromine nitrate appears in short, thick crystals and rhombs
which grow to masses and rosettes. The murexide test can readily
be performed on an object-glass, and the results are conclusive with
20 μg., and probably with less.

Mercuric Chloride.—To avoid confusion with the members proper
of this group, the following reactions for mercury may be per-
formed with the sublimates. Zinc chloroiodide gives a pale red
colour at the edges, and the precipitate is soluble in an excess of the
reagent. Hydriodic acid gives a brownish-red precipitate at the
rim, which is immediately soluble in excess of the reagent. Nitric
acid yields a colourless solution which, on evaporation, deposits long
prisms of mercuric chloride. Identification of mercuric chloride
is confirmed by the following tests: Precipitation of the iodide
from iodine solutions by means of copper sulphate, precipitation
of the oxide by alkali, amalgamation with copper wires under a
coverslip, distillation, and conversion of the distilled mercury into
the iodide.   H. W.

Use of Certain Reagents for the Detection of Emetine in Human Urine.

CH. MATTEI (*Compt. rend. Soc. Biol.*, 1918,
81, 315--317; from *Chem. Zentr.*, 1919, ii, 326).—The sensitive-
ness of a number of reagents has been determined, using emetine
solutions of known content. Tancret's reagent gives a perceptible
turbidity with 0·0000125 gram emetine hydrochloride in 5 c.c.,
Mayer-Valser's reagent with 0·000025 gram in 5 c.c., Dragendorff's
and Bouchardat's reagents with 0·00005 gram in 5 c.c. Calcium
chloride and hydrochloric acid give a distinct coloration with
0·0002 gram in 5 c.c. Froehde's reagent is also very sensitive.
                                                  H. W.

Detection of Nicotine.

O. TUNMANN (*Apoth. Zeit.*, 1918, 33,
485—486; from *Chem. Zentr.*, 1919, ii, 227).—A few crystals of
p-dimethylaminobenzaldehyde are dissolved in a drop of fuming
hydrochloric acid on an object-glass and brought into contact with
a drop of an aqueous solution of nicotine. A pink, and then a
reddish-violet, zone is formed at the line of contact, and the whole
liquid becomes reddish-violet. The coloration increases in intensity
and is permanent for ten to twenty-four hours. Under similar
conditions, coniine, pyridine, and acetone do not yield colorations.
Coniine, pyridine, and the other alkaloids do not influence the
reaction. Aniline, in not too dilute solution, gives a red coloration,
but crystals of the dye immediately separate. The reaction affords
the most sensitive test for nicotine without using a microscope, and
occurs within a minute with 0·2 mg. of the alkaloid. The presence
of nicotine in cigar smoke is easily demonstrated in this manner.

The most sensitive microchemical reagent is a cold saturated solution of picric acid to which 10% of concentrated hydrochloric acid has been added. A yellow, amorphous precipitate, from which crystals separate in a few seconds, which is recognisable with the naked eye, is obtained with 10 µg. nicotine. With 5 µg. of the alkaloid, the precipitate is not formed, but the same crystals appear, generally, however, in indistinct, feathery forms, but always of the same magnitude and arranged in groups. The latter can generally be recognised by the eye, invariably with a lens. The limit of sensitiveness (in two to three minutes) is 3 µg. The prismatic crystals shine yellow and green between crossed Nicols, and generally have oblique extinction. Aniline, coniine, and dilute pyridine do not yield crystals. Pure pyridine gives similar crystals, but not the preliminary amorphous precipitate.

H. W.

Identification of Bilirubin. E. KLAFTEN (*Wien. klin. Woch.*, 1918, **31**, 1018; from *Chem. Zentr.*, 1919, ii, 152).—Methylene-blue solution (1%, five drops) is added to the urine (5 c.c.), giving an emerald-green coloration, which disappears on addition of two to three drops of potassium permanganate solution (1%) and is replaced by an intense blue colour. The reaction is character-istic of bile pigments, and depends on their ready decomposition by potassium permanganate, whereby the yellow components are removed from the mixture of dyes.

H. W.

A System of Blood Analysis. OTTO FOLIN and HSIEN WU (*J. Biol. Chem.*, 1919, **38**, 81—110).—An attempt to combine a number of different analytical procedures into a compact system of blood analysis so that estimations of non-protein nitrogen, urea, creatinine, creatine, uric acid, and sugar may be carried out on 10 c.c. of blood. The pivotal point is the preparation of a satis-factory protein-free filtrate from the blood. For this purpose, tungstic acid was found highly satisfactory, less than 1 gram being sufficient to remove the proteins of 10 c.c. of blood. The separ-ation is rapid and does not involve any loss of the substances which it is desired to estimate. In this filtrate, total non-protein nitrogen is determined by a slight modification of the direct Nesslerisation method (A., 1916, ii, 573). Sugar is estimated by the reduction of an alkaline copper tartrate solution, followed by the measure-ment of the depth of colour produced with Folin's phenol reagen (A., 1912, ii, 1012). The results indicate that this method is the most accurate of any proposed for the estimation of blood sugar.

J. C. D.

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EXPERIMENTAL.

The results herein recorded were obtained during the course of an investigation which is still in progress (and, when completed, will form the subject of a communication to this Society), on the relative tendencies to spontaneous ignition of the several distinct portions into which a banded bituminous coal can be separated (see Stopes, *Proc. Roy. Soc.*, 1919, [*B*], **90**, 470; Tideswell and Wheeler, this vol., 619). The particular coal used was the "durain" portion of the Thick Coal Seam, Hamstead Colliery.

The apparatus used, which will be described in detail when the complete research is described, enabled air or oxygen or any mixture of gases to be circulated in a closed system through the coal, which was packed in a reaction-tube the temperature of which could be maintained constant. The progress of the reaction could be followed by the change of pressure within the system and by analysis of the gases.

In all but the experiments with mixtures of carbon monoxide and air, in which a water-bubbler was used, the gases were dried by passage through a calcium chloride tube included in the circuit. The coal was ground so as to pass through a 10×10 and remain on a 60×60 mesh sieve. At the beginning and end of each experiment the coal, in position in the reaction tube, was raised to 200° and exhausted at that temperature.

Typical results for the absorption of pure oxygen at different temperatures are recorded in Fig. 1. Typical results when mixtures of carbon monoxide and air and hydrogen and air were used are as follow:

Carbon Monoxide and Air (7·45 per cent. CO).

Volume of apparatus : 3,300 c.c.
Mean pressure of gases : 660 mm.
Composition: Expressed as c.c. at 15° and 760 mm.

	CO_2.	O_2.	CO.	N_2.	H_2.
Initial atmosphere.........	0·9	590	227	2240	nil
Final atmosphere (after circulation during 120 hours at 100°)............	53·4	79	249	2240	nil

Oxygen absorbed $= 511$ c.c. CO_2 formed $= 52·5$ c.c.
CO formed $= 22$ c.c.   Ratio $CO_2/CO = 2·4$.

	CO_2.	O_2.	CO.	N_2.	H_2.
Gases removed from the coal by exhaustion at 200°	26·5	nil	7·7	0·3	nil
Ratio CO_2/CO removed at 200°......................	3·3				

Hydrogen and Air (3·85 per cent. H₂).

Volume of apparatus : 1,200 c.c.
Mean pressure of gases: 560 mm.

Composition : Expressed as c.c. at 15° and 760 mm.

	CO₂.	O₂.	CO.	N₂.	H₂.
Initial atmosphere	nil	213·5	nil	788	40·2
After 20 hours at 100° ...	10·52	16·5	3·46	796	40·8
„ 42 „ „ ...	11·20	4·9	4·60	791	39·7
„ 66 „ „ ...	12·00	2·6	4·77	791	40·5

Oxygen absorbed=211 c.c.   CO₂ formed=12·0 c.c.
CO formed=4·77 c.c.   Ratio CO₂/CO=2·5.

	CO₂.	O₂.	CO.	N₂.	H₂.
Gases removed from the coal by exhaustion at 200°	3·7	nil	1·2	0·1	nil
Ratio CO₂/CO removed at 200°	3·1				

ESKMEALS,
CUMBERLAND.   [*Received, June 18th*, 1919.]

LXXVI.—*The Catalytic Reduction of Hydrogen Cyanide.*

By SYDNEY BARRATT and ALAN FRANCIS TITLEY.

WHEN hydrogen cyanide vapour is reduced by gaseous hydrogen in the presence of metallic catalysts, mono-, di-, and tri-methylamine, ammonia, and methane form the bulk of the products. The present paper deals with the relative quantities of the basic substances produced, which were found to vary with the nature and temperature of the catalyst, and with other conditions which are described.

Debus (*Journ. Chem. Soc.*, 1863, **16**, 249) passed a mixture of hydrogen and hydrogen cyanide over platinum black and noticed reduction, accompanied by a considerable development of heat, even at the ordinary temperature. He states that the reaction proceeded vigorously at 110°, the main product being monomethylamine. The rapid decrease in the activity of the catalyst was attributed by him to the formation of a double cyanide of methylamine and platinum, which he isolated.

Linnemann (*Annalen*, 1868, **145**, 38), using the same catalyst, found that the reduction proceeded smoothly at 300°. Although the formation of the double salt was not observed, he found that the catalyst soon lost its activity.

Sabatier and Senderens (*Compt. rend.*, 1905, **140**, 482) investigated the reduction of hydrogen cyanide in the presence of nickel.

They showed that the temperature required for efficient reduction lay between 300° and 400°, or somewhat higher than that required by other nitriles. Ammonia and dimethylamine preponderated in the products isolated.

<center>EXPERIMENTAL.</center>

The larger number of the results described in this paper were obtained with platinum catalysts, but preliminary experiments were also carried out with finely divided iron prepared by the decomposition of ferrous oxalate at 380°.

With the latter catalyst, reduction proceeded at 170° and upwards. At 200°, the basic products isolated by passing the resulting gases through hydrochloric acid contained approximately 45 per cent. of monomethylamine and 55 per cent. of ammonia, with barely a trace of dimethylamine.

The rate of reduction was very low, even at higher temperatures, and after trials under varying conditions, the conclusion was reached that iron was an unsuitable catalyst for the reduction of hydrogen cyanide.

Platinum proved to be considerably more efficient than iron as a catalyst for this reduction, and although it was not found possible to employ the low temperatures suggested by Debus, the activity displayed by the platinum at rather higher temperatures was consistent throughout a long series of experiments.
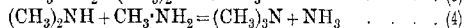
The catalyst was prepared by soaking blue asbestos fibre in platinum chloride solution. The resulting mass was then dried and reduced in a current of hydrogen at 150°. Catalysts containing from 0·1 to 40 per cent. of platinum on the asbestos were tested. Only those preparations containing more than 10 per cent. of platinum were of practical value in the form of apparatus described below. Those containing less platinum were not sufficiently vigorous, and the catalyst containing 20 per cent. of platinum was most frequently employed. Such variations in the composition of the catalyst affected only the efficiency of the reduction, and not the nature of the products.

Hydrogen cyanide dried by calcium chloride was prepared and liquefied, using the method described by Wade and Panting (T., 1898, **73**, 255); its vapour, mixed with a regulated volume of electrolytic hydrogen, was passed through 22—30 cm. of platinised asbestos in a 1·3 cm. tube heated in a resistance furnace to a temperature measured by a thermo-couple. The alkaline products of the reduction were retained by passage of the gases through hydrochloric acid.

<center>L L 2</center>

Under these conditions, reduction was first observed at 80°. The velocity of the reaction increases smoothly with rise of tempera- ture to 180°, above which it was fairly rapid; for example, at 200°, 90—100 per cent. of the total hydrogen cyanide in a mixture, passed at the rate of 6 litres an hour, was reduced by 0·3 gram of platinum on 1 gram of asbestos. There appeared to be no advantage in raising the temperature of the catalyst above 220°. The composition of the products, however, was not appreciably affected by carrying out the reduction above 250°.

The products were analysed by the following method. The hydrochloric acid solution of the amines and ammonia was evaporated to dryness, and the solid chlorides were extracted with a known volume of absolute alcohol in excess over that required for complete solution of the amine hydrochlorides. Allowance being made for the slight solubility of ammonium chlorides in alcohol, evaporation of the alcoholic solution gave the total weight of amine hydrochlorides present. These were finally extracted with chloroform to separate the mono- and di-methylammonium chlorides.

From a consideration of the following equations,

$$HCN + 2H_2 = CH_3 \cdot NH_2 \qquad \ldots \ldots \ldots \ldots (1)$$
$$HCN + 3H_2 = NH_3 + CH_4 \qquad \ldots \ldots \ldots \ldots (2)$$
$$2CH_3 \cdot NH_2 = (CH_3)_2NH + NH_3 \qquad \ldots \ldots \ldots (3)$$
$$(CH_3)_2NH + CH_3 \cdot NH_2 = (CH_3)_3N + NH_3 \qquad \ldots \ldots (4)$$
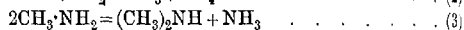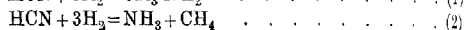
it will be seen that, in accordance with the law of mass action, reaction (2) might be expected to be favoured by an excess of hydrogen in the gas mixture passing the catalyst. The very reverse, however, took place. If the partial pressure of the hydrogen cyanide was high and approached that required in theory for complete utilisation of the hydrogen (that is, 1 vol. of hydrogen cyanide to 2 vols. of hydrogen), then the products consisted almost entirely of ammonia. As the partial pressure of the hydrogen cyanide decreased, however, the proportion of the methylamines in the product rapidly increased. This continued up to a maxi- mum, above which, however dilute a gas mixture was employed, the methylamine content of the product was constant. The following table and figure illustrate this point.

Composition of gas mixture.						Total methylamines, per cent.	Ammonia, per cent.
1 vol. HCN to 1¼ vols. H₂......						8	92
1	,,	,,	4	,,	,, ...	33	66
1	,,	,,	6	,,	,, ...	68	32
1	,,	,,	8	,,	,, ...	78	22
1	,,	,,	15	,,	,, ...	80	20

We are unable to offer an explanation of this anomaly.

The "total methylamines" given in the above table consist of mono- and di-methylamines in varying proportions, although tri-methylamine is also present in minute quantities. The proportion between mono- and di-methylamine, as would be expected, is also affected by the partial pressure of hydrogen cyanide in the react-ing gases. With a concentration of 1 vol. of hydrogen cyanide to 4 vols. of hydrogen, more than half of the total methylamine was dimethylamine. With 1 vol. of hydrogen cyanide to 15 vols. of hydrogen, this decreased to less than 10 per cent. of the total. This is shown in the accompanying figure (curve A).

| Composition of gas mixture.					Mono- and di-methylamine in the products. Per cent.	
					Mono-	Di-
1 vol. HCN to 4·0 vols. H₂ ...					10	25
1	,,	,, 4·4	,,	,, ...	15	23
1	,,	,, 5·6	,,	,, ...	40	20
1	,,	,, 6·3	,,	,, ...	54	16
1	,	,, 8·0	,,	,, ...	66	12
1	,,	,, 15·0	,,	,, ...	72	8

The figures given in the tables above vary within about 5 per cent. in individual experiments, made with different preparations of catalyst containing the same amount of platinum. The tables represent the results obtained with a catalyst prepared as described, and working at temperatures from 180° to 220°.

The alteration in the behaviour of the catalyst with use proved to be unusual. Although the formation of a double cyanide of platinum and methylamine, to which Debus attributed the short-lived activity of his platinum black, was never observed, the activity of our catalysts was found to undergo a peculiar change during successive experiments. The longer the time in use, in spite of identical conditions of temperature and gas concentration, the greater the percentage of ammonia in the reduction products became. This change was very irregular, but occurred more rapidly the less platinum there was on the asbestos. Thus with 0·4 gram of platinum deposited on 1 gram of asbestos, the com-position of the products was constant during a period of fifteen hours, but with only 0·1 gram of platinum to the same weight of asbestos, an appreciable difference was noticed after one hour.

Attempts to renew the original behaviour of the catalyst by heat-ing in hydrogen, oxygen, or hydrogen chloride up to 600° were unsuccessful. Treatment with chlorine, however, at 200° for a short period completely renewed the former activity, and, in one or two cases, brought about a slight increase in the yield of methyl-

amine over that obtained with the freshly prepared platinum. In one case, the original percentage of methylamines in the products was 79; during five hours' use of the same catalyst, this decreased to 50, but, after passage of chlorine over the platinum, rose to 86 at the same temperature and with the same concentration of the gases.

Graph illustrating the changes in the products of reduction caused by alterations in the composition of the gas mixture.

Volumes of hydrogen to one volume of hydrogen cyanide.
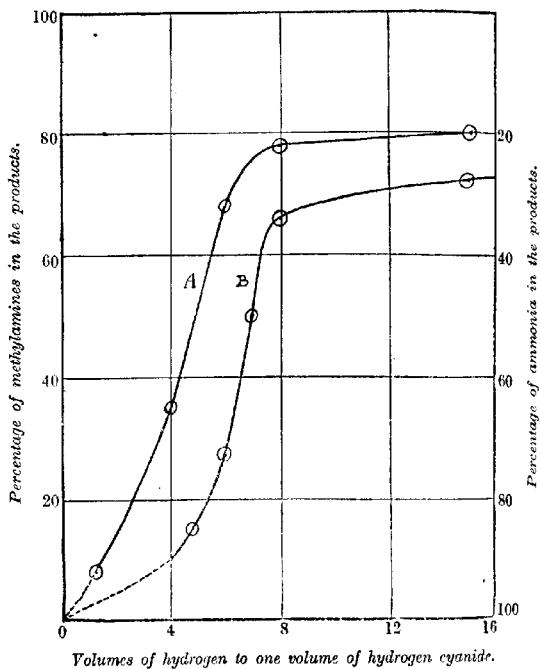
A. *Percentage of methylamine.*

B. *Percentage of monomethylamine.*

At the close of the above work, the conditions were briefly studied, under which methylamine decomposes into hydrogen and hydrogen cyanide.

Liquid monomethylamine was prepared from the hydrochloride and sodium hydroxide, and its vapour passed over a platinum catalyst, prepared as described. It was found that the dehydrogen-

ation, although perceptible at 220°, only proceeds with consider-able velocity above 300°, that is, at temperatures more than 100° higher than the minimum required for efficient hydrogenation of the cyanide. This is in accordance with the general rule observed by Sabatier.

Since ammonia and methane, as well as hydrogen cyanide and dimethylamine, were detected in the products, it appears probable that the hydrogen resulting from the dehydrogenation process reduces a further portion of the methylamine (compare Sabatier and Mailhe, *Compt. rend.*, 1917, **165**, 224, 309).

Summary.

(1) Platinum catalyses the reduction of hydrogen cyanide by gaseous hydrogen above 120°, readily above 180°.

(2) The nature of the reduction products, although unaffected by alterations of temperature between 120° and 250°, is dependent on the partial pressure of the hydrogen cyanide in the gas mixture employed, the proportion of monomethylamine increasing to a maximum as this partial pressure is decreased. The secondary reactions which give rise to di- and tri-methylamine are also less marked the lower the pressure of the hydrogen cyanide.

If the concentration of the hydrogen cyanide in the gas mixture is made sufficiently small, a yield of 80 per cent. of total methyl-amines, and more than 70 per cent. of monomethylamine, can be obtained.

(3) On continued use of a given catalyst, the yield of methyl-amine diminishes, and is replaced by ammonia. The original behaviour of the platinum is restored by treatment with chlorine.

(4) The dehydrogenation and auto-reduction of methylamine only proceeds with noticeable velocity above 300° in the presence of platinum, and was not observed at 200°, the temperature employed in the majority of the experiments described in this communication.

LXXVII.—*The Chemistry of Burgundy Mixtures.*

By ROBERT LUDWIG MOND and CHRISTIAN HEBERLEIN.

ALTHOUGH mixtures of sodium carbonate and copper sulphate, generally known as " Burgundy mixtures," have been in use for a number of years as a most effective agent for combating plant diseases of a fungoid character, the chemical reactions which take place when these substances are mixed in solution have hitherto not received much attention.

Abegg ("Handbuch der anorg. Chemie," II., i, 633) states: " From solutions of copper sulphate, sodium carbonate at ordinary temperatures gives a greenish-blue colloidal precipitate of varying composition, which contains absorbed alkali carbonate. With excess of copper sulphate the precipitate also contains basic copper sulphate. With equivalent quantities of the components the gel contains copper and carbon dioxide in the ratio $2CuO : 1CO_2$.

If the precipitates are left with the mother liquor they become crystalline and change into the green, granular basic carbonate, $3CuCO_3,3Cu(OH)_2,H_2O$.

In contact with a concentrated solution of sodium carbonate, the gel is transformed into Deville's blue, crystalline double carbonate, $Na_2CO_3,CuCO_3,3H_2O$."

This statement pointed to a complexity of reactions which required further elucidation. The fact that a colloidal solution was formed appeared to us to have an important bearing on the fungicidal properties of the material in question, and we asked Prof. Barker, of the University of Bristol, to investigate the relative advantages of the colloidal over the crystalline state. His preliminary results are embodied in a very interesting paper, which will be published in the University's Annual Report.

In spite of the highly significant work which has been done by Pickering (T., 1909, **95**, 1409) and Ravaz ("Le Mildion," Paris, Masson and Cie., 1914) on Burgundy mixture, we found the problem more complicated than they had assumed, and we proceeded to carry out our investigations on the following lines:

(1) The main reactions between copper sulphate and sodium carbonate were quantitatively studied with various ratios of the components.

(2) The reaction between copper sulphate and sodium hydrogen carbonate was examined.

(3) The free carbon dioxide and the carbon dioxide in the precipitate were estimated, and the ratio $CuO : CO_2$ in the precipitate was determined.

(4) The solvent action of carbonic acid was studied.

(5) The basic sulphate was determined in various mixtures to ascertain the ratio $CuO : SO_3$ and $CuO : CO_2 : SO_3$.

(6) The absorbed sodium carbonate was estimated.

(7) The causes and reactions of the change from the colloidal precipitate to malachite were investigated.

(1) *The Main Reactions between Copper Sulphate and Sodium Carbonate.*

The mixtures were generally made at 15° by dissolving 4 grams of crystallised copper sulphate in 200 c.c. of water and a varying amount of crystallised sodium carbonate in 200 c.c. of water, and then pouring the two solutions simultaneously into a third beaker, thus avoiding any excess of one reagent over the other. The mixtures were tested (*a*) with litmus paper; (*b*) the copper in solution was estimated by electrolysis; (*c*) a filtered portion of the mixture was tested directly with ferrocyanide; (*d*) a filtered portion, after boiling and filtering, was tested with ferrocyanide; (*e*) the free sodium hydrogen carbonate and the basic copper sulphate in solution were titrated with $N/10$-hydrochloric acid, using methyl-orange as indicator; (*f*) the free sodium carbonate was titrated with phenolphthalein as indicator.

The various mixtures and the results of the analyses are tabulated in table I.

It will be noticed that a theoretical mixture of equivalent amounts of copper sulphate and sodium carbonate, namely, 4 grams of $CuSO_4,5H_2O$: 4·58 grams of $Na_2CO_3,10H_2O$, although reacting alkaline towards litmus and methyl-orange, contains a considerable amount of copper in solution. A mixture with 7·38 grams of sodium carbonate (Pickering's mixture) contains the minimum amount of soluble copper. Larger amounts of sodium carbonate cause the formation of complex compounds containing electronegative copper.

From curve 1 in Fig. 2 it will be seen that the solution is alkaline towards methyl-orange after a small addition of sodium carbonate, due to soluble basic copper sulphate. The curves in this figure show three distinct stages. Up to 4·25 grams of sodium carbonate the solution contains free copper sulphate and an increasing amount

L L*

TABLE I.

| Copper sulphate. Grams.	Crystalline sodium carbonate. Grams.	Molecular ratio, $CuSO_4 : Na_2CO_3$.	Litmus reaction.	Potassium ferrocyanide. After filtration.	Potassium ferrocyanide. After boiling.	Copper in solution. Grams per litre.	Copper in solution. Per cent. on total.	Titration with $N/10$-HCl. for Na_2CO_3, c.c.	Titration with $N/10$-HCl. for $NaHCO_3$, c.c.	In solution in total mixture. Na_2CO_3, grams.	In solution in total mixture. $NaHCO_3$, grams.	Percentage in solution. as Na_2CO_3.	as $NaHCO_3$.	as Na_2CO_3 (+).	as $NaHCO_3$ (+).
4·0	2·13	1 : 0·46	acid	Cu	Cu	1·240	50·22	—	0·22	—	—	—	—	—	—
4·0	3·18	1 : 0·70	,,	,,	,,	0·72	29·16	—	0·38	—	—	—	—	—	—
4·0	4·15	—	neutral	,,	,,	—	—	—	0·59	—	0·1982	—	7·9	—	7·9
4·0	4·20	—	,,	,,	trace Cu	—	—	—	0·68	—	0·2413	—	9·7	—	9·7
4·0	4·25	1 : 0·93	faintly alkaline	,,	nil	0·24	9·6	—	0·64	—	0·2150	—	8·6	—	8·6 { standard mixture.
4·0	4·50	1 : 0·98	,,	,,	,,	0·20	8·0	—	0·81	—	0·2645	—	10·0	—	10·0
4·0	5·0	1 : 1·10	distinctly alkaline	,,	,,	0·12	4·8	—	1·29	—	0·4389	—	14·9	—	14·9
4·0	6·38	1 : 1·39	,,	,,	,,	0·04	1·6	—	3·12	—	1·080	—	28·8	—	28·8
4·0	7·38	1 : 1·62	,,	,, trace Cu	,,	0·005	0·2	—	4·63	—	1·5946	—	36·8	—	36·8
4·0	7·45	—	,,	,,	,,	—	—	—	4·54	—	—	—	—	—	—
4·0	7·52	—	strongly alkaline	,,	,,	—	—	0·10	4·57	—	—	—	—	—	—
4·0	7·59	—	,,	,,	,,	—	—	0·15	—	—	—	—	—	—	—
4·0	7·66	—	,,	Cu	Cu	—	—	0·15	4·75	—	—	—	—	—	—
4·0	7·94	—	,,	,,	,,	—	—	0·43	4·84	—	—	—	—	—	—
4·0	8·5	1 : 1·86				0·01	0·4	1·64	4·84	0·3347	1·6669	10·6	31·6		42·2
4·0	12·75	1 : 2·79				0·02	0·8	7·81	5·46	1·6971	1·8804	35·9	25·1		61·0

TABLE I (continued).

Copper sulphte. Grams.	Crystalline sodium carbonate. Grams.	Molecular ratio. $CuSO_4 : Na_2CO_3$.	Litmus reaction.	Potassium ferrocyanide. After filtration. Cu	Potassium ferrocyanide. After boiling. Cu	Copper in solution. Grams per litre.	Copper in solution. Per cent. on total.	Titration with $N/10$-HCl. for Na_2CO_3. C.c.	Titration with $N/10$-HCl. for $NaHCO_3$. C.c.	In solution in total mixture. Grams Na_2CO_3.	In solution in total mixture. Grams $NaHCO_3$.	Percentage as Na_2CO_3.	Percentage as $NaHCO_3$.	+	Na_2CO_3 as $NaHCO_3$.	
4·0	17·0	1 : 3·72	strongly alkaline	—	—	0·08	3·2	13·99	6·19	3·0400	2,1318	48·2	21·3		89·5	after mixing.
4·0	4·25	1 : 0·93	—	—	—	0·22	—	—	0·58	—	0·1973	—	7·9		7·9	after passing CO_2 for 30 minutes.
—	—	—	—	—	—	0·36	—	—	1·11	—	0·3776	—	15·1		15·1	after keeping in CO_2 for 1 day.
—	—	—	—	—	—	0·42	—	—	1·18	—	—	—	—		—	after passing air free from CO_2 for 1 hour.
4·0	4·25	1 : 0·93	—	—	—	0·02	—	—	0·10	—	—	—	—		—	after passing ordinary air for 1 hour.
4·0	4·25	1 : 0·93	—	—	—	0·04	—	—	0·10	—	—	—	—		—	after boiling filtrate.
4·0	4·25	—	—	—	—	nil	—	—	0·98	—	0·0370	—	1·6		1·6	2 per cent. mixtures.
4·0	4·5	—	—	—	—	0·20	—	—	1·22	—	0·1008	—	3·8		3·8	
4·0	5·0	—	—	—	—	0·12	—	—	2·04	—	0·5715	—	19·5		19·5	

of dissolved basic copper sulphate. From 4·25 to 7·38 grams the dissolved basic copper sulphate falls to a minimum. The sodium hydrogen carbonate rises regularly from nil, and beyond 7·38 grams of sodium carbonate free sodium carbonate appears.

Copper sulphate solution, as is well known, has an acid reaction, due to its tendency to form basic salts by hydrolysis. If the free

Fig. 1.

Grams of crystalline sodium carbonate.
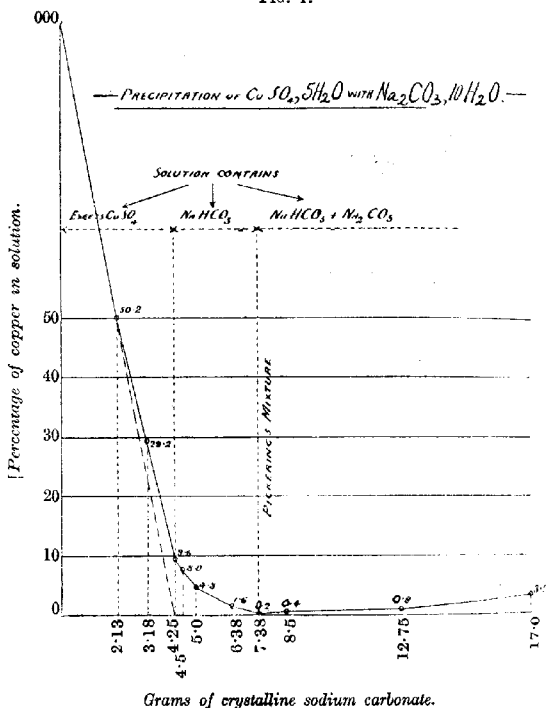
acid is neutralised by sodium carbonate, the solution will remain neutral or alkaline so long as the basic sulphate is kept in solution by the carbon dioxide evolved. With the gradual loss of the latter, the basic sulphate becomes insoluble, and further hydrolysis takes place until the solution is again acid. Further addition of sodium carbonate neutralises this acid, carbon dioxide is evolved, part of the

basic sulphate is precipitated, part of it is retained in solution by the carbon dioxide, and all these reactions are repeated until the whole of the copper sulphate is converted. The formation of basic copper sulphate is thus simply explained, and it is clear that a temporarily neutral solution can be obtained with very little sodium carbonate. A permanently neutral solution is obtained with 4·25

Fig. 2.

Grams of crystalline sodium carbonate.
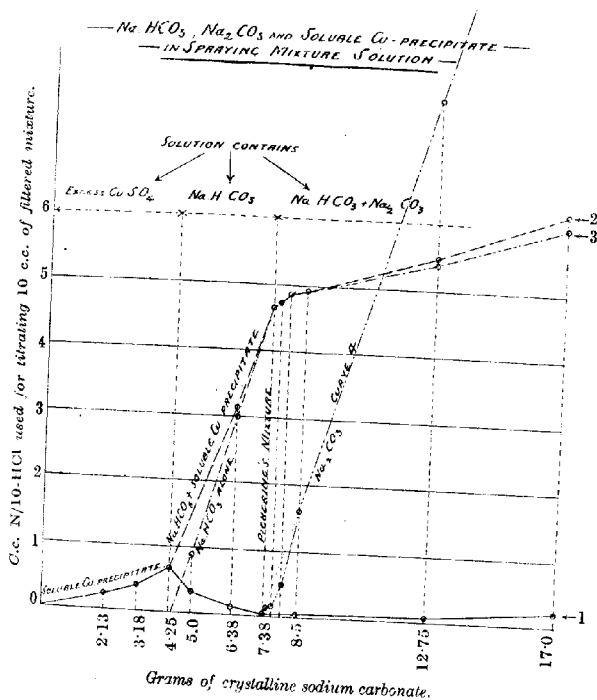
grams of sodium carbonate, which is less than the theoretical amount, because hydrolysis performs its share in the precipitation.

The sodium carbonate, besides neutralising the free acid, acts on the basic sulphate, converting it partly into basic carbonate. The carbon dioxide thus evolved increases the solubility of the basic sulphate, and with 4·25 grams of sodium carbonate the maximum

amount of free carbon dioxide and of dissolved basic sulphate is reached. Above 4·25 grams the excess of sodium carbonate is converted into hydrogen carbonate, the amount of carbon dioxide decreases, and proportionate amounts of basic sulphate are precipitated. At 7·38 grams of sodium carbonate all carbon dioxide has disappeared and the minimum of dissolved basic copper sulphate is reached. Above 7·38 grams the solution contains also normal carbonate, which forms soluble complex copper compounds, as is shown in the rising curve of soluble copper.

We have therefore established that the complete conversion of 4 grams of crystallised copper sulphate is effected with 4·25 grams of crystallised sodium carbonate, that is, 92·8 per cent. of the theoretical quantity. Such a mixture reacts neutral towards red litmus paper, faintly acid towards blue litmus (owing to the free carbon dioxide), and alkaline towards methyl-orange. If the mixture is filtered, the filtrate, which will contain 9·6 per cent. of the total copper as soluble basic sulphate, gives a heavy, red precipitate with ferrocyanide. This is due to the secondary action of the carbon dioxide, and the test is therefore misleading. If, however, the carbon dioxide is eliminated, either by a current of air or by boiling, and then the ferrocyanide test applied, no trace of copper can be detected in solution.

As this mixture of copper sulphate and sodium carbonate contains no free copper sulphate and no free alkali, carbonate or hydrogen carbonate, but, on the other hand, the maximum of dissolved basic copper sulphate, it may be regarded as having not only the highest fungicidal efficiency, but also a maximum potentiality to cause injury to foliage. This is borne out by Prof. Barker's experiments, and in the field.

Physical examination of our mixture showed that the copper precipitate, as well as the dissolved basic sulphate, is in the colloidal condition. The sodium sulphate mother liquor can be separated from the dissolved basic sulphate by dialysis. On removal of the carbon dioxide the hydrosol of basic copper sulphate separates as well, the reaction being easily reversible.

As is well known, Burgundy mixture changes after a while from a colloidal into a crystalline condition, giving rise to a number of chemical reactions which will be examined hereafter.

The addition of 0·02 per cent. of glue was found to be most effective in prolonging the period during which the colloidal state exists.
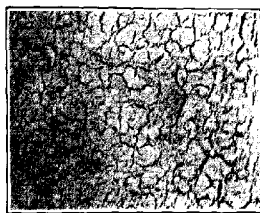
The three micro-photographs illustrate the drying of a colloidal film; (a) is without glue; (b) with glue; and (c) is without glue,
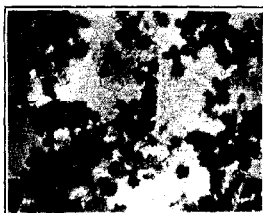
Colloidal
(A) *Without glue.*
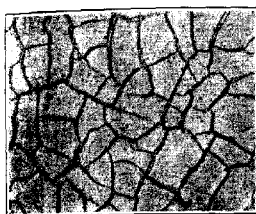
Colloidal
(B) *With glue.*

Magnified

Magnified.

Crystalline.
(C) *Without glue*

Magnified.

showing the change to the crystalline state. The separate crystals of malachite and sodium sulphate are clearly distinguishable.

(2) *The Reaction between Copper Sulphate and Sodium Hydrogen Carbonate.*

We found that the reaction between copper sulphate and sodium hydrogen carbonate proceeds similarly to the case of the normal carbonate; basic sulphate and basic carbonate are formed, carbon dioxide is set free, and a similar amount of basic sulphate is dissolved. The minimum weight of sodium hydrogen carbonate for complete conversion is 2·50 grams or 92·6 per cent. of the theoretical. This figure is close to the figure 92·8 found for the normal carbonate, and here also the hydrogen carbonate acts not as a direct precipitating agent, but as a neutralising agent. The copper precipitate obtained with the hydrogen carbonate has a paler blue colour, it separates out sooner from the mother liquor, being less hydrated, and contains $Cu = 21·02$; $CO_2 = 5·67$ per cent., and has a ratio $CuO : CC_2 = 2·56 : 1$.

(3) *Estimation of Carbon Dioxide in the Copper Precipitate, and of the Free Carbon Dioxide.*

TABLE II.

		Carbon dioxide evolved, per cent.	Percentage of carbon dioxide on total carbon dioxide. = 100 per cent.
Crystalline sodium carbonate plus sulphuric acid ... ... grams of CuSO$_4$,5H$_2$O + 4·25 grams of crystalline sodium carbonate	on boiling	15·1	100
,, ,,	15°	7·87 } 7·95 }	Average = 52·4
,, ,,	60°	9·78	64·8
,, ,,	on boiling	15·10	100·0

TABLE III.

Showing the Molecular Ratio $CuO:CO_2$ in the Precipitate.

No.	Mixture.	After.	Percentage in precipitate. CuO.	CO_2.	Mol. ratio. $CuO:CO_2$	
1	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$	½ hour. colloid.	5·10	1·58	2·26 : 1	Filtered, not washed.
2	,,	1 day. ,,	6·10	1·85	2·28 : 1	
3	,,	1½ days. ,,	6·10	1·68	2·51 : 1	
4	,,	2 ,, ,,	6·10	1·53	2·76 : 1	
5	,,	½ hour. ,,	7·91	2·43	2·25 : 1	Filtered and washed twice.
6	,,	3 hours. ,,	7·91	2·32	2·36 : 1	
7	,,	4 days. ,,	7·91	2·26	2·42 : 1	
8	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$ and glue	1 hour ,,	7·67	2·42	2·19 : 1	Washed.
9	,,	36 days. ,,	6·76	1·35	3·46 : 1	,,
10	4 grams of $CuSO_4,5H_2O$ + 7·38 grams of $Na_2CO_3,10H_2O$ ...	1 hour. ,,	7·54	2·36	2·21 : 1	,,
11	4 grams of $CuSO_4,5H_2O$ + 2·125 grams of $Na_2CO_3,10H_2O$ ...	,, ,,	4·20	1·26	2·30 : 1	,,
12	4 grams of $CuSO_4,5H_2O$ + 1·0625 grams of $Na_2CO_3,10H_2O$ ...	,, ,,	4·68	0·42	7·7 : 1	,,

TABLE III *(continued).*

Showing the Molecular Ratio $CuO : CO_2$ in the Precipitate.

No.	Mixture.	After.		Percentage in precipitate		Mol. ratio.	
				CuO.	CO_2.	$CuO : CO_2$	
13	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$ at 60°	1 hour	crystalline	—	—	2·93 : 1	Sprayed on glass and dried.
14	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$ at 80°	,,	,,	8·99	0·83	7·5 : 1	
·5	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$ at 15°	7 days.	,,	31·89	7·51	2·94 : 1	
16	4 grams of $CuSO_4,5H_2O$ + 4·25 grams of $Na_2CO_3,10H_2O$	4 ,,	,,	15·96	2·88	3·84 : 1	Filtered, washed, and stirred with water.
17	,,	22 ,,	,,	47·89	8·33	3·97 : 1	
18	,,	8 ,,	,,	11·35	3·06	2·57 : 1	Passing air through for 2 hours. Left until crystalline.
19	,,	7 ,,	,,	23·65	5·08	3·22 : 1	As above, but air freed from CO_2.
20	,,	7 ,,	,,	19·53	3·79	3·56 : 1	In stoppered bottle.
21	,,	18 ,,	,,	33·5	11·9	1·95 : 1	Saturated CO_2.
22	,,	5 ,,	,,	23·8	8·39	1·99 : 1	
23	,,	5 ,,	,,	27·3	9·46	2·00 : 1	
24	,,	1½ ,,	,,	24·58	4·14	4·11 : 1	Filtered, stirred with NaHCO₃ solution.
25	4 grams of $CuSO_4,5H_2O$ + 2·45 grams of NaHCO₃	1 hour.	colloid	21·02	5·67	2·56 : 1	

The average ratio in a 4·25 mixture is $CuO : CO_2 = 2·25 : 1$. Experiments 1 to 7 show that the copper precipitate, when formed quickly loses carbon dioxide, the ratio altering gradually. On keeping the mixture in an open vessel, carbon dioxide is liberated by the decomposition of the basic copper carbonate and the precipitate becomes crystalline. It is not yet evident, however, from these experiments that the change of the colloidal to the crystalline state is due to any alteration of the ratio $CuO : CO_2$.

Fresh colloidal mixtures have the ratio $CuO : CO_2 = 2·26 : 1$.
Old crystalline mixtures have the ratio $CuO : CO_2 = 2·94 : 1$.
Old crystalline mixtures saturated with carbon dioxide $= 2·00 : 1$.
Old colloidal mixtures and glue have the ratio $CuO : CO_2 = 2·46 : 1$.

(4) *The Solvent Action of Carbonic Acid.*

An examination of the constitution of the dissolved basic copper compound present in acid, neutral, and alkaline mixtures has proved to us that only basic copper sulphate is dissolved by the carbon dioxide. Reference to curve 1 in Fig. 2 shows that the amount of copper precipitate dissolved by carbon dioxide rises gradually to a maximum containing 4·25 grams of sodium carbonate, then falls to its lowest point at 7·38. This maximum of dissolved copper corresponds with 9·6 per cent. of the total copper and is equal to 0·24 gram of copper per litre in a 1 per cent. mixture. By saturat-

TABLE IV.

Time.	Mixture 1 without glue. Soluble copper per litre. Gram.	Mixture 2 with glue. Soluble copper per litre. Gram.
After mixing	0·26	0·30
1 hour	—	0·22
2 hours	0·22	—
4　,,　...........	0·22	—
1 day	0·22	0·22
2 days	0·22	—
3　,,　...............	0·22	—
5　,,　...............	0·16	—
6　,,　...............	—	0·16
7　,.　...............	0·10	—
	(precipitate begins to change)	
9　,　...............	0·06	0·10
10　,,　...............	0·06	—
11　,,　...............	0·06	0·10
13 ·　,,　...............	0·02	0·10
14　,,　...............	0·00	—.
16　,,　...............	—	0·06
20　,,　...............	—	0·02
22　,,　...............	—	0·01
24　,,　...............	—	nil

ing such a mixture with carbon dioxide the amount of soluble copper can be raised to 0·36 gram per litre. On the other hand, a mixture of 4 grams of crystallised copper sulphate and 8·5 grams of crystallised sodium carbonate containing 0·04 gram of copper per litre on being saturated with carbon dioxide shows scarcely any more soluble copper (0·06 gram per litre). The amount of basic copper sulphate in such a mixture being very small, the carbon dioxide finds little to dissolve, thus affording further proof that the copper carbonate is not dissolved by the carbon dioxide.

If an ordinary mixture, containing 4·25 grams of crystalline sodium carbonate, is allowed to remain in an open vessel, carbon dioxide is gradually evolved, and the amount of dissolved basic copper sulphate decreases in proportion. Table IV (p. 918) illustrates this.

After fourteen days an ordinary mixture containing 4·25 grams of crystalline sodium carbonate shows no more soluble copper and the precipitate has all turned to malachite. A similar mixture with 0·02 per cent. of glue loses its soluble copper more slowly, and after twenty-four days is still blue and colloidal.

(5) *The Basic Sulphate in the Copper Precipitate.*

TABLE V.

Mixture.		Sulphur in precipitate on total sulphur in mixture, = 100 per cent.	Copper precipitated. Per cent.	Molecular ratio, $CuO : SO_3$,
$CuSO_4$, $5H_2O$.	Na_2CO_3, $10H_2O$.			
4	0·2688	2·10	6·25	2·8 : 1
4	0·5375	3·7	12·5	3·2 : 1
4	1·075	6·9	25·0	3·5 : 1
4	2·15	14·7	50·0	3·2 : 1
4	3·2256	22·4	75·0	3·3 : 1
4	3·7632	21·5	87·5	4·0 : 1
4	4·0320	17·1	93·75	5·3 : 1
4	4·30	6·3	100·0	15·0 : 1
4	5·375	4·3	100·0	22·4 . 1
4	6·45	3·2	100·0	30·9 : 1
4	8·60	0·75	100·0	126·0 : 1
4	4·30	10·10	100·0	9·6 : 1

(precipitated at 80°)

Basic sulphate is found in every mixture. With small amounts of sodium carbonate, more basic sulphate is found than basic carbonate. With an increasing amount of sodium carbonate the ratio $CuO : SO_3$ keeps fairly constant for a time. The ratio in our mixture is 15 : 1. Whereas the ratio $CuO : CO_2$ shows little difference in varying mixtures, the ratio $CuO : SO_3$ alters greatly in mixtures containing an excessive amount of sodium carbonate, and the SO_3

disappears almost completely in a mixture containing 8·6 grams of sodium carbonate.

Treatment with saturated aqueous carbon dioxide decreases the SO_3 in the precipitate, and sodium hydrogen carbonate dissolves the SO_3 completely.

The ratio $CuO : SO_3$ in the soluble basic copper sulphate was found to be 3·5 : 1.

(6) *Estimation of the Absorbed Sodium Carbonate in the Copper Precipitate.*

On examining the titration figures in table I it will be noticed that the amount of sodium carbonate and hydrogen carbonate found in solution of the mixtures with an excessive amount of sodium carbonate ranges from 4·5 to 7·8 per cent. below the amount calculated. This can only be accounted for by its being absorbed by the precipitate. A direct estimation of the alkali in the precipitate was made and the above figures were confirmed.

TABLE VI.

Mixture	Na_2CO_3 in precipitate on total soda used, $=100$ per cent.	Mol. ratio $CuO : Na_2CO_3$ in precipitate.
4 grams of $CuSO_4,5H_2O + 4·25$ grams of $Na_2CO_3,10H_2O$ ...	4·0	73·5 : 1
4 grams of $CuSO_4,5H_2O + 4·25$ grams of $Na_2CO_3,10H_2O$ with glue	4·1	75·3 : 1
4 grams of $CuSO_4,5H_2O + 8·5$ grams of $Na_2CO_3,10H_2O$ ...	6·8	44·4 : 1

(7) *Causes of the Change from the Colloid to Malachite.*

Our experiments suggest that the colloidal state of the precipitate is dependent on the presence therein of sodium carbonate. The absorbed alkali is given up after some time and passes into solution, wherein it can be titrated.* The presence of an excessive amount of sodium carbonate in solution prevents this; a copper precipitate washed completely and stirred with sodium carbonate solution maintains its colloidal state indefinitely.

For the same reasons spraying mixtures with free sodium carbonate in solution (mixtures with more than 7·38 grams of sodium carbonate) retain the colloidal condition. Glue seems to act in a similar protective way.

Free carbon dioxide and sodium hydrogen carbonate destroy the

* When the maximum amount of free alkali in solution is reached, the change of the colloidal precipitate to the crystalline begins to be visible.

colloidal compound, the former acting on the absorbed sodium carbonate, forming hydrogen carbonate, the latter acting on the SO_3-groups, thus decomposing the compound.

A mixture containing 4·25 grams of crystallised sodium carbonate kept in an open vessel at 15° changes to malachite in seven days. Acid mixtures with less sodium carbonate or alkaline mixtures with less than 7·38 grams of sodium carbonate change sooner.

The presence of glue in every case retards the change.

Conclusions.

(1) On mixing copper sulphate with sodium carbonate solution three distinct copper compounds are formed : (a) Insoluble hydrated basic copper carbonate, which forms the bulk of the precipitate; (b) insoluble hydrated basic copper sulphate; and (c) soluble basic copper sulphate. Complete conversion of copper sulphate into these salts is obtained when for 1 molecule of copper sulphate 0·93 molecule of sodium carbonate is added, or for 4 grams of crystallised copper sulphate, 4·25 grams of crystallised sodium carbonate ($Na_2CO_3,10H_2O$).

(2) Judging by the results obtained, there appears to be no well-defined compound of copper, the composition altering according to conditions of precipitation. All the copper compounds are subject to rapid changes, the basic copper carbonate losing carbon dioxide and the dissolved basic copper sulphate soon becoming insoluble.

(3) A 1 per cent. mixture of 4 grams of copper sulphate and 4·25 grams of crystallised sodium carbonate made at 15° gives

(a) Basic copper carbonate containing CuO and CO_2 in the ratio 2·2 : 1.

(b) Insoluble basic copper sulphate containing CuO and SO_3 in the ratio 15 : 1.

(c) Soluble basic copper sulphate equal to 9·6 per cent. of the total copper present.

(4) On making the mixture at 15° free carbon dioxide is evolved, equal to 52·4 per cent. of the total carbon dioxide present in the sodium carbonate.

(5) At a higher temperature more carbon dioxide is evolved, until on reaching boiling point all carbon dioxide is expelled and the copper precipitate is converted into black copper hydroxide.

(6) The amount of basic copper sulphate formed is dependent on the amount of sodium carbonate used, and decreases as the latter is increased.

(7) The free carbon dioxide acts as a solvent on the basic copper sulphate only, not on the basic copper carbonate.

(8) The maximum of soluble basic copper sulphate is obtained in a mixture of 4 grams of copper sulphate and 4·45 grams of crystallised sodium carbonate for the reason that this mixture gives the maximum of free carbon dioxide.

(9) With larger amounts of sodium carbonate free carbon dioxide is neutralised to form sodium hydrogen carbonate.

(10) A mixture with 7·38 grams of crystallised sodium carbonate contains no more free carbon dioxide, and therefore a minimum of soluble basic copper sulphate.

(11) The copper precipitate at 15° contains absorbed sodium carbonate in the ratio $CuO : Na_2CO_3 = 74 : 1$.

(12) The whole of the copper precipitate is at first colloidal. After a short or long period, according to the temperature and the ratio of the ingredients in the mixture, the gel changes to the crystalline state.

(13) Addition of 0·02 per cent. of glue prolongs the life of the gel.

(14) Presence of free copper sulphate, or sodium hydrogen carbonate, or carbonic acid in the mixture accelerates the change of the colloidal to the crystalline state, whereas normal sodium carbonate helps to maintain the colloidal condition.

(15) The dissolved basic copper sulphate is in the form of hydrosol.

(16) The colloidal state of the precipitate appears to be conditional on the absorbed sodium carbonate.

(17) This absorbed sodium carbonate is found in the solution after some time, whereupon the change of the colloid to the crystalline begins to be visible.

(18) Changes in the sulphur content of the copper precipitate also take place during the change of the colloid to the crystalloid.

(19) The crystalline precipitate contains less carbon dioxide than the colloid. The ratio of $CuO : CO_2$ in old crystalline precipitate is found to be 2·94 : 1.

From the results obtained in this research it is apparent that the chemistry of "Bungundy mixture" is of a much more complex nature than previously suspected, and there are a number of questions which have to be further elucidated. The nature of the colloid solution and the conditions of its formation and change to the crystalline state await further investigations, and the influence produced by small quantities of glue indicates the importance of making further experiments with similar colloids.

MOND NICKEL CO. RESEARCH LABORATORY.

LXXVIII.—*Examination of the Bark of* Croton gubouga. *Isolation of* 4-*Hydroxyhygric Acid* .

By JOHN AUGUSTUS GOODSON and HUBERT WILLIAM BENTLEY CLEWER.

Croton gubouga, S. Moore, is a small tree growing on the low veldt in the Eastern Transvaal near the Sabi and Selati rivers. The bark of the tree has a considerable local reputation among the natives as a remedy for malaria, and both the seeds and the bark have been used by Captain Maberley in conjunction with opium in the treatment of malarial fever (*Lancet*, 1899, **157**, 874).

A preliminary examination of the bark and the seeds has been made by Mr. H. H. Green, B.Sc., in South Africa (private communication), who found that the ground bark caused purgation and emesis in dogs, but that rabbits were less sensitive to its action, although in doses of 1 gram per kilogram of body-weight it induced diarrhœa. In human beings administration of the bark according to Mr. Green causes an intense burning sensation in the throat, salivation, and slight nausea, with, in some cases, a slight laxative effect. The seeds exert a similar action. Mr. Green further observed that the acrid substance to which these effects are ascribed is extracted to some extent by hot water, and readily by ether.

The bark has also been examined by Greenish (*Pharm. J.*, 1918, **101**, 289), who found that the acrid constituent was largely extracted by hot light petroleum as well as by ether, chloroform, or alcohol.

For the material used in the present investigation the authors are indebted to Mr. I. B. Pole Evans, Chief of the Division of Botany, Union of South Africa.

The bark had a slight but not unpleasant odour. Dust from the ground bark caused sneezing and produced a burning sensation in the throat and on the tongue. It has not been possible to isolate the acrid constituent to which the irritant properties of the bark are due, in a form suitable for investigation, and it is possible that the seeds, which it is hoped to examine shortly, may prove more suitable for this purpose. The present paper deals chiefly with an acid isolated from the bark, which has proved to be a new optically active hydroxyhygric acid.

Preliminary Examination.

When extracted with Prollius' fluid the ground bark yielded a trace of alkaloid and furnished the following percentages of extract when exhausted in a Soxhlet apparatus with solvents in the order named: petroleum (b. p. 35—60°), 3; ether, 0·7; chloroform, 0·3; ethyl acetate, 0·8; alcohol, 4·3; total, 9·1.

Petroleum Extract.—This extract, on treatment with ether, left only a trace of insoluble matter. The solution yielded only traces of material to aqueous solutions of ammonium and potassium carbonates, but potassium hydroxide solution extracted a quantity of brown potassium salt, from which fatty acids (*A*), equivalent to 21 per cent. of the original extract, were recovered.

The solution left after the removal of the fatty acids contains the acrid constituent of the bark, but the authors have not yet been able to isolate this in a condition suitable for investigation (compare Greenish, *loc. cit.*). Hydrolysis, by alkalis, as described below, destroyed this acrid constituent.

The neutral material was hydrolysed by boiling for one hour with potassium hydroxide in alcoholic solution, after which the solution was concentrated, mixed with water, and extracted with ether to remove unsaponifiable matter. This, amounting to 20 per cent. of the original extract, included only a trace of hydrocarbon, or higher aliphatic alcohol, and consisted of semi-solid matter, from which a phytosterol was isolated, which gave a well-marked Liebermann reaction and on acetylation yielded a substance melting at 117°, probably a mixture of acetyl derivatives.

The remaining alkaline liquid was acidified with sulphuric acid, and the mixture distilled in a current of steam, when a yield of about 3·4 per cent. of volatile acids was obtained. The distillate was dissolved in an excess of barium hydroxide solution, the excess of baryta removed by carbon dioxide, and the filtrate concentrated. On adding silver nitrate solution to this liquid, silver was immediately precipitated; moreover, the solution instantly decolorised permanganate, indicating the presence of formic acid. On further concentration a quantity of a sparingly soluble barium salt separated. This was removed and converted into the acid, which was then dissolved in a slight excess of sodium hydroxide, and a silver salt prepared:

0·0413 gave 0·0178 Ag. Ag = 43·1.

$C_8H_{15}O_2Ag$ (silver *n*-octoate) requires Ag = 43·0 per cent.

The aqueous solution of the barium salts from which the above-described acid was separated still contained formic acid, and in

order to remove it, the solution was acidified, shaken with ether, and the ethereal solution well washed with water. In this way a further quantity of acid was obtained, which was fractionally converted into silver salts and the five fractions obtained were analysed:

1. 0·1315 gave 0·0665 Ag. Ag = 50·6.
2. 0·1817 „ 0·0934 Ag. Ag = 51·4.
3. 0·1448 „ 0·0744 Ag. Ag = 51·4.
4. 0·0951 „ 0·0490 Ag. Ag = 51·5.
5. 0·0273 „ 0·0141 Ag. Ag = 51·7.

$C_5H_9O_2Ag$ (silver valerate) requires Ag = 51·6 per cent.

The volatile acids present in the plant appear, therefore, to include formic, valeric, and n-octoic acids.

The acid liquid which had been distilled in a current of steam was extracted with ether, and the dark-coloured residue digested twice with petroleum. This left undissolved a dark-coloured, amorphous, resinous substance. The solution when concentrated gave a 23 per cent. yield of fatty acids, which were mixed with the 21 per cent. of free acids (A) previously obtained (see above). The acids were converted into lead salts, which from their behaviour appeared to be a mixture of lead salts of saturated and unsaturated fatty acids.

Ethereal Extract.—This consisted of a dark green resin, which on digestion with ether left a quantity of a light coloured substance undissolved. This was almost insoluble in the usual organic solvents except pyridine, from a dilute solution in which it separated in microscopic crystals melting at about 250° and giving the Liebermann reaction, whence it appeared to be a phytosterolin. The ethereal solution was then extracted first with water, removing about 10 per cent. of the extract, and finally with potassium hydroxide solution, which extracted 36 per cent. of acidic resin, leaving neutral resin; none of these yielded any crystalline material.

Chloroform and Ethyl Acetate Extracts.—These extracts consisted of amorphous resins. From the chloroform extract there separated gradually a fawn-coloured material, which was not obtained crystalline, nor could a crystalline acetyl derivative be prepared from it.

Alcoholic Extract.—This extract was redissolved in alcohol and water added, which precipitated a quantity of a nearly black tar. The clear liquid was treated with an excess of basic lead acetate, the precipitate filtered off, and the lead removed from the precipitate and filtrate by means of hydrogen sulphide in the usual way. The concentrated liquid from the former gave a nearly black colour with

ferric chloride and contained tannin. The concentrated filtrate was evaporated to complete dryness, and finally digested on the water-bath with nine successive portions of about 50 c.c. each of absolute alcohol to separate the large quantity of reducing sugars present. Each fraction was poured from the syrupy residue while hot, and when cold, again poured from a small amount of separated syrup, which was returned to the larger bulk. Crystals separated from each fraction when kept, but only a small quantity from the last. The whole amount of crystalline matter accumulated weighed about 6 grams. This substance proved to be 4-*hydroxyhygric acid*, an optically active acid not previously described.

Examination of the Acid.

To obtain sufficient material for the identification of the acid, further quantities of the bark were extracted, when the following varying percentage yields were obtained: 0·41, 0·21, and 0·25, amounting in all to 16·35 grams of crude acid.

The product may be readily purified by boiling its solution in water with animal charcoal, repeatedly concentrating the filtrate under diminished pressure with additions of alcohol, until the pure acid separates from the hot solution in colourless needles or prisms, which contain varying amounts of water of crystallisation, thus:

 I. 0·1986 lost 0·0170 at 110°. $H_2O = 8·56$.

 II. 0·2108 ,, 0·0108 ,, 110°. $H_2O = 5·13$.

Although the acid is very readily soluble in water it may be crystallised from that solvent. 7·05 Grams of substance were dissolved in water, and the solution was concentrated until about 4·5 grams of water remained. The solution was seeded and allowed to remain overnight, when 1·25 grams of the acid had separated in crystals, which appeared to be truncated prisms. These crystals, after being dried in the air, were found to contain one molecule of water:

0·2035 lost 0·0220 at 110°. $H_2O = 10·8$.

  $C_6H_{11}O_3N,H_2O$ requires $H_2O = 11·0$ per cent.

 I. 0·1324 * gave 0·2402 CO_2 and 0·0938 H_2O. $C = 49·5$; $H = 7·9$.

 II. 0·1090 * ,, 0·1976 CO_2 ,, 0·0778 H_2O. $C = 49·5$; $H = 8·0$.

0·1474 gave 12·6 c.c. N_2 at 17° and 746 mm. $N = 9·7$.

  $C_6H_{11}O_3N$ requires $C = 49·6$; $H = 7·6$; $N = 9·7$ per cent.

Methoxyl estimation: 0·1751 gave no AgI. MeO = 0.

N-*Methyl estimation:* 0·1751 ,, 0·2430 AgI. NMe = 17·2.

  $C_5H_8O_3N·CH_3$ requires NMe = 20·0 per cent.

* Dried at 105°.

The acid decomposes with effervescence at 242°, possesses little if any taste, is acid to litmus, but cannot be titrated, is not hygroscopic, and is optically active.

The specific rotatory power was determined in water of (a) a specimen of the acid crystallised from alcohol and containing $H_2O = 5·13$, and (b) a specimen crystallised from water and containing $H_2O = 10·8$ per cent. :

(a) $c = 4·9910$, $l = 1$-dcm., $a_D - 4·02°$; $[a]_D - 80·5°$ or $[a]_D - 84·9°$ for the anhydrous substance.

(b) $c = 5·2300$, $l = 1$-dcm., $a_D - 3·98°$; $[a]_D - 76·2°$ or $[a]_D - 85·4°$ for the anhydrous substance.

It gives a strong pyrrole reaction, and dissolves copper oxide with the formation of a copper salt. A quantity (0·2 gram) of the substance was dissolved in water, and the solution boiled for several hours with an excess of powdered copper oxide, the excess of copper oxide filtered off, and the filtrate concentrated. Blue prisms separated, which were dried on a porous tile, washed with 70 per cent. alcohol, and dried in the air :

0·1021 lost 0·0200 at 110°. $H_2O = 19·6$.

$C_{12}H_{20}O_6N_2Cu,4H_2O$ requires $H_2O = 17·0$; $C_{12}H_{20}O_6N_2Cu,5H_2O$ requires $H_2O = 20·4$.

0·0669 (anhydrous salt) gave 0·0146 CuO.   Cu = 17·4.

$C_{12}H_{20}O_6N_2Cu$ requires Cu = 18·1 per cent.

Constitution of the Acid from Croton gubouga *Bark.*

The evidence already given indicates that the substance is a 4-hydroxy-1-methylpyrrolidine-2-carboxylic acid (4-hydroxyhygric acid). Two such compounds have been synthesised by Leuchs and Felser (*Ber.*, 1908, **41**, 1726), namely, two optically inactive forms of 4-hydroxy-1-methylpyrrolidine-2-carboxylic acid. A comparison of the principal properties of these acids with that from *C. gubouga* bark is given in the following table :

	Formula.	$[a]_D$.	M. p.	Reaction.	Taste.
Acid from Croton bark	$C_6H_{11}O_3N$	−85·4°	242°	faintly acid.	little or no taste.
a - 4 - Hydroxy - 1 - methylpyrrolidine-2-carboxylic acid...................	$C_6H_{11}O_3N$	inactive.	207–208°	neutral.	marked sweet taste
b - 4 - Hydroxy - 1 - methylpyrrol idine-2-carboxylic acid	$C_6H_{11}O_3N$	inactive.	226–227°	faintly acid.	sweetish insipid taste.

Comparison of the specific rotations of the closely related pyrrol-idine derivatives indicates that in all probability this acid from Croton bark is 4-hydroxyhygric acid (γ-hydroxy-N-methylproline):
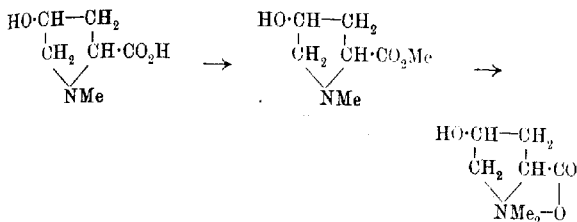
$$\begin{array}{ccc}
\underset{\underset{\text{NH}}{\overset{\displaystyle\text{CH}_2\cdot\text{CH}_2}{\diagup\diagdown}}}{\text{CH}_2\ \ \overset{*}{\text{CH}}\cdot\text{CO}_2\text{H}} &
\underset{\underset{\text{NMe}}{\overset{\displaystyle\text{CH}_2\cdot\text{CH}_2}{\diagup\diagdown}}}{\text{CH}_2\ \ \overset{*}{\text{CH}}\cdot\text{CO}_2\text{H}} &
\underset{\underset{\text{NMe}_2\text{–O}}{\overset{\displaystyle\text{CH}_2\cdot\text{CH}_2}{\diagup\diagdown}}}{\text{CH}_2\ \ \overset{*}{\text{CH}}\cdot\text{CO}}
\end{array}$$

l-Proline (natural) (Fischer), [a]ᵤ –77·4°.	Hygric acid; active form does not appear to have been isolated.	*l*-Stachydrine (natural), [a]ᴅ of hydrochloride –26·5° (Yoshimura and Trier).

$$\begin{array}{ccc}
\underset{\underset{\text{NH}}{\overset{\displaystyle\overset{*}{\text{HO}\cdot\text{CH}}-\text{CH}_2}{\diagup\diagdown}}}{\text{CH}_2\ \ \overset{*}{\text{CH}}\cdot\text{CO}_2\text{H}} &
\underset{\underset{\text{NMe}}{\overset{\displaystyle\overset{*}{\text{HO}\cdot\text{CH}}-\text{CH}_2}{\diagup\diagdown}}}{\text{CH}_2\ \ \overset{*}{\text{CH}}\cdot\text{CO}_2\text{H}} &
\underset{\underset{\text{NMe}_2\text{–O}}{\overset{\displaystyle\overset{*}{\text{HO}\cdot\text{CH}}-\text{CH}_2}{\diagup\diagdown}}}{\text{CH}_2\ \ \overset{*}{\text{CH}}\cdot\text{CO}}
\end{array}$$

l-Hydroxyproline (Fischer), [a]ₒ –81·1° (natural) (Leuchs and Brewster), [a]ₒ –76·3° (synthetic).	Formula suggested for acid from Croton bark, [a]ᴅ –85·4° (natural).	Betonicine hydrochloride, [a]ᵤ –24·79° (natural); hydrochloride, [a]ᴅ –24·1° (synthetic).	Turicine (natural), hydrochloride [a]ᵤ +24·65°.

(Küng and Trier).

Leuchs and Brewster (*Ber.*, 1913, **46**, 986) have synthesised *l*-hydroxyproline, and Küng (*Zeitsch. physiol. Chem.*, 1913, **85**, 217) on methylating this substance obtained a mixture of the betaines, betonicine and turicine. If, therefore, the acid from *Croton gubouga* bark is in reality 4-hydroxyhygric acid it should in like manner, on methylation, give betonicine and turicine. Küng's method of methylation, with slight modification, was adopted, and resulted in the production of a mixture of betonicine and turicine, thus proving the acid to be 4-hydroxyhygric acid.

Küng (*loc. cit.*) has pointed out that turicine and betonicine are not enantiomorphs. When *l*-hydroxyproline or *l*-hydroxyhygric acid is methylated, using methyl iodide and alkali, it is probable that racemisation occurs and that one of the carbon atoms only, namely, that attached to the carboxyl group, is concerned in the racemisation. It will be interesting to see whether optically active hygric acid, which so far does not appear to have been obtained, and will only possess one asymmetric carbon atom, will yield on methylation two stereoisomeric betaines.

It seemed possible that methylation of the hydroxyhygric acid might be accomplished without racemisation if the use of alkali were avoided, and so evidence might be secured as to which of the

betaines, betonicine or turicine, corresponds with l-hydroxyproline and 4-hydroxyhygric acid. It was hoped that by passing hydrogen chloride into boiling methyl alcohol containing 4-hydroxyhygric acid the methyl ester would first be formed, and would pass into the corresponding betaine, thus :

$$HO\cdot CH\text{---}CH_2$$
$$\begin{array}{cc} | & | \\ CH_2 & CH\cdot CO_2H \\ & \diagdown\diagup \\ & NMe \end{array} \longrightarrow$$

$$HO\cdot CH\text{---}CH_2$$
$$\begin{array}{cc} | & | \\ CH_2 & CH\cdot CO_2Me \\ & \diagdown\diagup \\ & NMe \end{array} \longrightarrow$$

$$HO\cdot CH\text{---}CH_2$$
$$\begin{array}{cc} | & | \\ CH_2 & CH\cdot CO \\ & \diagdown\diagup \quad | \\ & NMe_2\text{---}O \end{array}.$$

It is probable that the ester was formed, but was rapidly hydrolysed, since on treating the hydrochloride with silver oxide the original 4-hydroxyhygric acid was recovered unchanged.

Methylation of the Acid.

A preliminary experiment was carried out, using 1 gram of the acid, which was dissolved in a mixture of 2 c.c. of water and 20 c.c. of methyl alcohol. Five c.c. of a solution of 6 grams of potassium hydroxide in 100 c.c. of methyl alcohol, and a like quantity of a solution of methyl iodide in methyl alcohol (3 grams in 20 c.c.), were added alternately 1 c.c. at a time. As the solution remained alkaline, a further 5 c.c. of the methyl iodide solution were added, and the mixture boiled on a water-bath for half an hour. One c.c. of methyl iodide was then added and sufficient methyl-alcoholic potassium hydroxide to render the liquid alkaline. The solution was boiled for about twenty minutes and made alkaline, again boiled for five minutes and made alkaline, and the operation repeated until the alkalinity persisted. The alcohol was distilled off, the residue dissolved in water, the solution made slightly acid with hydrochloric acid, and boiled with excess of silver chloride. The silver iodide and excess of silver chloride were filtered off, and the filtrate evaporated to dryness under diminished pressure. The residue was treated with absolute alcohol and again evaporated to dryness. The dry residue was extracted with five small quantities of boiling absolute alcohol; the first three of which removed all but traces of the hydrochlorides of the betaines. The alcohol was distilled off and the rotation of the residue determined, using water as solvent ($c = 6\cdot4275$, $l = 1$-dcm., $\alpha_D + 0\cdot075°$; $[\alpha]_D + 1\cdot2°$).

This result indicated that the methylation had proceeded as expected, and that a mixture of turicine and betonicine hydrochlorides in about equal amounts had been produced.

Küng and Trier (*loc. cit.*) pointed out the difficulty of separating turicine and betonicine by fractional crystallisation of their hydrochlorides, and recommended for this purpose the free bases. This the authors are able to confirm, since on dissolving the mixed hydrochlorides having $[a]_D +1.2°$ in absolute alcohol, concentrating and allowing to crystallise, 0·667 gram of a mixture of rosettes of needles, and rosettes of plates was obtained which gave $[a]_D +3°$ ($c = 3.335$, $l = 1$-dcm., $a_D +0.10°$), and on further recrystallisation a mixture of crystals amounting to 0·456 gram and having $[a]_D +5.0°$ ($c = 2.280$, $l = 1$-dcm., $a_D 0.115°$) was obtained. The various solutions were united, the alcohol was removed by distillation under diminished pressure, and the free bases were liberated by treating the aqueous solution with excess of silver oxide. The silver chloride and excess of silver oxide were filtered off, the filtrate was concentrated, absolute alcohol added, and the solution again concentrated, this operation being repeated until crystals separated out on cooling. 0·137 Gram of substance crystallised in long prisms, which had a sweet taste, decomposed at 250° with frothing, and gave $[a]_D + 21.2°$ ($c = 2.6400$, $l = 1$-dcm., $a_D + 0.58°$).

Five grams of the acid were then methylated as described above with slight modifications. The same proportions of methyl iodide, methyl-alcoholic potassium hydroxide and acid were used, but the solutions were more concentrated. The alcoholic solution of the mixed hydrochlorides from the extraction of the dried mixture of potassium chloride and betaine hydrochlorides was kept overnight to separate as much potassium chloride as possible. When the hydrochlorides had been converted into bases by treating their aqueous solution with silver oxide and the silver chloride and undissolved excess of silver oxide removed by filtration, hydrogen sulphide was passed through the solution of the bases to remove any silver in solution. The solution of the betaines was concentrated to low bulk under diminished pressure, alcohol added, and the solution again concentrated; this operation was repeated until crystallisation set in on cooling. From the mother liquor two further crops were obtained on concentration.

Crop I consisted of nearly pure turicine, amounting to 1·7 grams. The air-dried substance was examined polarimetrically in water:

$$c = 2.5330,\ l = 1\text{-dcm.},\ a_D + 0.87°;\ [a]_D + 34.3°.$$

On recrystallisation until the optical rotation was constant, the value $[a]_D + 40.9°$ was obtained for the anhydrous substance.

Crop II weighed 1·2 grams and was a mixture:

$$c = 2\cdot5840, \; l = 1\text{-dcm.}, \; \alpha_D - 0\cdot48°; \; [\alpha]_D - 18\cdot6°.$$

Crop III, weighing 1·06 grams, was also a mixture:

$$c = 2\cdot6180, \; l = 1\text{-dcm.}, \; \alpha_D - 0\cdot41°; \; [\alpha]_D - 15\cdot7°.$$

Crops II and III were united, converted into hydrochlorides, dissolved in absolute alcohol, and the solution was concentrated, when 1·45 grams of nearly pure betonicine hydrochloride crystallised out:

$$c = 3\cdot3765, \; l = 1\text{-dcm.}, \; \alpha_D - 0\cdot75°; \; [\alpha]_D - 22\cdot2°.$$

As it was found difficult to remove all traces of potassium chloride from the betonicine hydrochloride, and it was not possible to obtain a higher value than $[\alpha]_D - 22\cdot9°$ on recrystallising this particular specimen, a further methylation of the acid was tried with good results, using sodium hydroxide instead of potassium hydroxide; with this difference, 3·9 grams of the acid were methylated as in the previous experiment; 1·2731 grams of crude turicine were obtained as a first crop:

$$c = 6\cdot3655, \; l = 1\text{-dcm.}, \; \alpha_D + 2\cdot25°; \; [\alpha]_D + 35\cdot3° \text{ for the anhydrous}$$
substance.

The bases in the mother liquor were converted into hydrochlorides, and crystallised from absolute alcohol; 1·322 grams of nearly pure betonicine hydrochloride were obtained, having $[\alpha]_D - 22\cdot7°$ ($c = 6\cdot6100, \; l = 1\text{-dcm.}, \; \alpha_D - 1\cdot50°$). This was recrystallised until its optical rotation remained constant, the highest reading being $[\alpha]_D - 24\cdot8°$ ($c = 3\cdot5900, \; l = 1\text{-dcm.}, \; \alpha_D - 0\cdot89°$).

The bases in the mother liquor from the betonicine hydrochloride ($[\alpha]_D - 22\cdot7°$) were regenerated by treatment with silver oxide. On crystallisation from alcohol a further 0·4012 gram having $[\alpha]_D + 4\cdot0°$ ($c = 2\cdot0060, \; l = 1\text{-dcm.}, \; \alpha_D + 0\cdot08°$) was obtained.

The formation of a mixture of turicine and betonicine by the methylation of the acid from *Croton gubouga* bark leaves no doubt that the acid is 4-hydroxyhygric acid, as formulated on p. 928.

Properties of Turicine.

Turicine crystallises from alcohol in flat prisms containing one molecule of water of crystallisation, which it rapidly loses in a vacuum desiccator. It is neutral to litmus, is not hygroscopic, has a sweet taste, and gives an intense pyrrole reaction. The anhydrous substance decomposes with frothing at 260°, as did a specimen kindly supplied by Prof. A. Küng; the decomposition point was not depressed on mixing the two specimens. The hydrated substance commenced to melt at about 249°, but finally decomposed with frothing at 256°. Prof. Küng's specimen, and a mixture of the

two, behaved in the same way. (Found, $H_2O = 10·59$; $C_7H_{13}O_3N,H_2O$ requires $H_2O = 10·17$. Found, $C = 52·7$; $H = 8·3$. $C_7H_{13}O_3N$ requires $C = 52·8$; $H = 8·2$ per cent.)

The specific rotations of three specimens of the anhydrous substance were determined in water:

I. $c = 1·8065$, $l = 1$-dcm., $α_D + 0·75°$; $[α]_D + 41·5°$.

II. $c = 1·3950$, $l = 1$-dcm., $α_D + 0·57°$; $[α]_D + 40·9°$.

III. $c = 2·0980$, $l = 1$-dcm., $α_D + 0·85°$; $[α]_D + 40·5°$.

Küng and Trier give $[α]_D + 36·26°$ for the hydrated betaine corresponding with $[α]_D + 40·4°$ for the anhydrous substance.

Turicine Hydrochloride.—This was prepared from the pure base. When crystallised rapidly from absolute alcohol it separated in needles, but when allowed to crystallise slowly, six-sided tablets were obtained. It is acid to litmus, and decomposes with frothing at 224°; Küng and Trier give 222° and 223° as the melting and decomposing point. Its specific rotation was determined in water. $c = 2·8000$, $l = 1$-dcm., $α_D + 0·72°$; $[α]_D + 25·7°$. Küng and Trier give $[α]_D + 24·65°$, and state that turicine is not hygroscopic, but the authors are of the opinion that it is slightly hygroscopic.

Turicine aurichloride was obtained by adding gold chloride solution to a concentrated aqueous solution of turicine hydrochloride. The crystals, which separated rapidly, were collected, dissolved in hot water, and the solution was allowed to cool, when the double chloride crystallised in clusters of yellow prisms. The decomposition point was determined in the same bath with a specimen of turicine aurichloride kindly supplied by Prof. Küng, and a mixture of the two specimens; the decomposition with frothing occurred in each case at 230—232°. Küng and Trier give the melting and decomposing point as 232°. (Found, $Au = 39·0$; $C_7H_{13}O_3N,HAuCl_4$ requires $Au = 39·5$ per cent.)

Properties of Betonicine.

The free base was obtained from the pure hydrochloride by treating with silver oxide. It crystallises anhydrous from alcohol in short, four-sided, truncated pyramids, is more readily soluble in alcohol than turicine, has a sweet taste, is neutral to litmus, and gives an intense pyrrole reaction. Küng and Trier state that it is not hygroscopic, and that it melts and decomposes at 243—244°; the purest specimen obtained by the authors was slightly hygroscopic and decomposed with frothing at 252°. (Found, $C = 52·7$; $H = 8·5$. $C_7H_{13}O_3N$ requires $C = 52·8$; $H = 8·2$ per cent.) The specific rotation was determined in water:

$$c = 3·5050, l = 1\text{-dcm.}, α_D - 1·23°; [α]_D - 35·1°.$$

Küng and Trier give $[\alpha]_D - 36\cdot6°$.

Betonicine hydrochloride crystallises from absolute alcohol in needles or prisms, which, after drying at 105°, decompose with frothing at 227°; a specimen supplied by Prof. Küng, which was slightly coloured, after drying at 105°, decomposed with frothing at 224°; a mixture of the two specimens decomposed at an intermediate temperature. Küng and Trier give the melting and decomposing point as 222—223°. The hydrochloride is not hygroscopic and is acid in reaction. The specific rotatory power was determined in water:

$$c = 3\cdot5900,\ l = 1\text{-dcm.},\ \alpha_D - 0\cdot89°;\ [\alpha]_D - 24\cdot8°.$$

Küng and Trier give $[\alpha]_D - 24\cdot79°$ for natural betonicine hydrochloride, and Küng $[\alpha]_D - 24\cdot1°$ for his synthetic product.

Betonicine Aurichloride.—To a concentrated solution of betonicine hydrochloride a solution of gold chloride was added. There was no immediate separation of crystals as in the case of turicine hydrochloride. The solution was accordingly concentrated and, on cooling, four-sided, yellow plates crystallised out. When redissolved in hot water and kept, clusters of yellow tablets were obtained. The substance decomposed with frothing at 230—232°, the same temperature as a specimen supplied by Prof. Küng, and a mixture of the two specimens also decomposed at this point. (Found, Au = 39·2. $C_7H_{13}O_3N,HAuCl_4$ requires Au = 39·5 per cent.)

The authors desire to take this opportunity of thanking Prof. Küng for his kindness in supplying them with specimens of turicine, turicine aurichloride, betonicine hydrochloride, and betonicine aurichloride for comparison.

LXXIX.—*Harmine and Harmaline. Part III.*

By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

IN 1912 the present authors, having located in the harmine molecule a methyl group similarly situated to that in quinaldine, suggested that the alkaloid contains a fused ring system comprising a benzene, pyrrole, and pyridine nucleus, and constructed a constitutional formula (T., **101**, 1775) which satisfied the requirements of the facts then known. This expression (I) was discarded by O. Fischer (*Ber.*, 1914, **47**, 99) in favour of the formula II on account of his

discovery that harminic acid * may be oxidised by nitric acid in a sealed tube with the formation of *isonicotinic* acid (III), and this observation was held to be inconsistent with the assumption made in I that there is an imino-group attached to the pyridine ring:


(I.)   (II.)
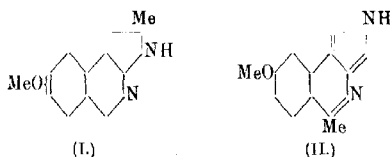
As the result of a further examination of derivatives of harmine and harmaline we are now convinced that neither of these formulæ is correct, and, after a careful reconsideration of the whole subject, have deduced fresh expressions which it is believed are more satisfactory representations of the chemistry of these bases. The argument which has been developed may be presented in the following sections.

The Ring System of Harmine and its Derivatives.

Harmine, $C_{13}H_{12}ON_2$, contains a methyl and a methoxyl group and may be written $C_{11}H_6N_2Me \cdot OMe$, and is therefore a derivative of a substance, $C_{11}H_8N_2$. Although the methoxyl and methyl groups have been separately eliminated with the production of compounds called harman and norharmine respectively, the parent, $C_{11}H_8N_2$, which might be called *norharman*, has not yet been prepared. Now harmaline, which is dihydroharmine, yields *m*-nitro-anisic acid (IV) on oxidation with nitric acid (O. Fischer and Boesler, *Ber.*, 1912, **45**, 1934), whilst the production of *isonicotinic* acid has already been referred to above. The existence of both benzene and pyridine nuclei in norharman is therefore certain, and, on inspection of the composition, it will be seen that there is no alternative to the theory that this substance must contain a benzene, pyridine, and pyrrole nucleus fused together as are the benzene nuclei in anthracene or phenanthrene. So much was already recognised, and in addition that the benzene nucleus occupies a terminal position in the system, a fact which follows from the consideration of the relation of harminic acid to harmine. It is neces-

* This acid is obtained from harmine by oxidation with chromic acid (O. Fischer and E. Tauber, *Ber.*, 1885, **18**, 403).
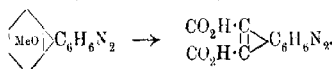
sary to recall these points in order to develop the present discussion.

When a compound containing a fused ring system is energetically oxidised, it is usual to be able to recognise, in the product, residual groups which are derived from the nucleus destroyed by the oxidation and are situated at both the points of fusion of the original rings. Yet, in the degradation of harmine, this rule is not followed in the two cases which have been already mentioned, namely, the production of nitroanisic acid from harmaline (or nitroharmaline) and that of *iso*nicotinic acid from harminic acid. In both these reactions one of the positions of ring fusion is represented by a hydrogen atom in the oxidation product. It will be necessary to assume the possibilities shown under *A* or *B* below, and these are clearly the only alternatives:

(III.)

A.   (IV.)   B.
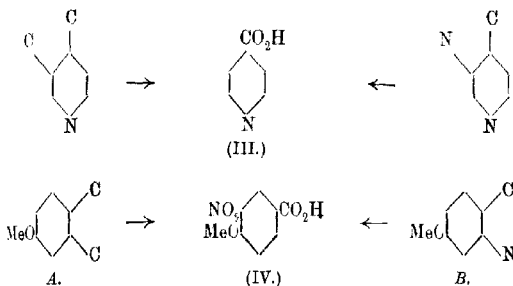
In attempting to make a choice from these alternatives, neither of which is quite in accord with previous experience, we have been guided by two main considerations. The first is that the conditions of elimination of carbon from direct union with aromatic nuclei are much better understood than those governing the similar removal of nitrogen, and whereas experimental and other evidence is not at present available to enable us to refute the alternative *B*, we are on much firmer ground in regard to *A*, which we consider is opposed to experience. O. Fischer suggested that a nitromethoxyphthalic acid is the intermediate product in the oxidation of harmaline, and that this loses carbon dioxide with the formation of nitroanisic acid. The supposed intermediate product does not, however, appear to have been isolated, and we can find no record in the literature of an analogous reaction in which a phthalic acid at all similarly constituted loses one of its carboxyl groups under comparable conditions. In the production of *iso*nicotinic acid scheme *A* makes it necessary to assume the elimination of carbon

M M 2

attached to the β-position in a pyridine nucleus, whilst that in the γ-position remains in the form of a carboxyl group. When it is remembered that, of the three pyridinemonocarboxylic acids, it is only nicotinic acid which requires to be heated with soda-lime in order to convert it into pyridine, and, further, that quinolinic acid and cinchomeronic acid both yield nicotinic acid on being strongly heated, it will be realised how relatively firm is the attachment of carbon to the β-position. It is consequently very improbable from this point of view that a pyridine derivative convertible into isonicotinic acid by a simple oxidation process can have a carbon atom attached to the β-position. The second argument in favour of the assumption that these degradations involve the elimination of nitrogen, and not of carbon, from direct combination with the surviving nuclei, is that we have obtained experimental indications that the benzene nucleus of a harmine derivative is actually directly attached to a nitrogen atom. Tetrahydroharmine, $C_{13}H_{16}ON_2$, condenses with diazobenzenesulphonic acid with the formation of a sparingly soluble, crystalline, orange - yellow azo - compound, $C_{13}H_{15}ON_2 \cdot N_2 \cdot C_6H_4 \cdot SO_3H$, which dyes silk yellow from an acid bath, behaves as an indicator, and undergoes changes with acid and alkali closely resembling those characteristic of methyl-orange. Comparison with a large number of azo-derivatives of various types derived from diazobenzenesulphonic acid and such second components as dihydroberberine, anhydrocryptopine, β-dialkylamino-crotonic esters, β-diketones, pyrrole, α- and β-methylindole and indole, showed that the change from yellow to crimson is exhibited only by the true benzeneazobenzene derivatives. It would therefore appear that tetrahydroharmine is an aniline derivative with a free para-position, and naturally the argument applies to all the bases of the group so far as it throws light on their nuclear structure. We are therefore compelled to accept this surprising elimination in a nitric acid oxidation of a side-chain commencing with a nitrogen atom, and in attempting to form an idea as to the possible mechanism of the reaction the clue seems to be given by the oxidation of phenylhydrazine with the production of benzene. Possibly, the imino-group of harmine becomes converted into the nitroamino- or nitrosoamino-group, and one of these becomes reduced by readily oxidisable groups produced in the course of the reaction, so that, at a certain stage, the condition is reached at which nitrogen is eliminated and hydrogen replaces the whole side-chain. Accepting scheme B and its implications, it is quite clear that if harmine contains no carbon attached to its pyridine nucleus in the β-position, this nucleus cannot be fused with a benzene ring and harmine cannot be a derivative of quinoline or isoquinoline. The order of

fusion of rings is, then, benzene–pyrrole–pyridine, and the methyl group must be in the pyridine nucleus. Further, the only possible formulæ for harmine, bearing in mind the formation of nitroanisic acid from harmaline, are the following:

(V.)   (VI.)   (VII.)
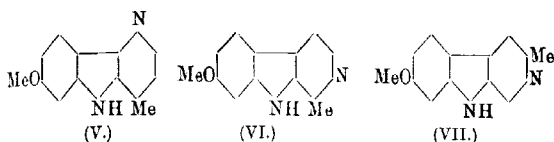
In V the methyl group is in the γ-position in the pyridine ring, and this is inconsistent with the behaviour of harmine, which, as we have already stated, closely resembles quinaldine in its reactions. It shows the quinophthalone reaction and condenses with benzaldehyde to benzylideneharmine, a styryl derivative, which may be oxidised to norharminecarboxylic acid (T., 1912, **101**, 1784). The latter gives a red coloration with ferrous sulphate, and easily loses carbon dioxide, on heating in glycerol, with the formation of norharmine. We therefore reject the structure V, and consider harmine must be either VI or VII, and since these differ only in the position attributed to the methyl group, the constitution of norharmine is determined and is shown in VIII:

(VIII.)
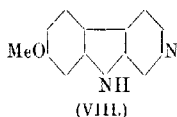
The Constitution of Harmine.

The decision between formulæ VI and VII for harmine is a difficult one, and cannot at present be made with precision, but there are strong indications which cause us to much prefer the former alternative. A glance at the structure of norharmine will show that it is a species of *iso*quinoline in which indole takes the place of benzene. Alkaloids of the *iso*quinoline group are known which contain a methyl group in their pyridine or reduced pyridine rings, and of these corydaline has been most completely investigated. The methyl group in VI is in the position which an analogy to corydaline would suggest. Further light is thrown on the problem by the study of the oxidation of *N*-methyltetrahydroharmine, and some preliminary remarks must be made in regard to the constitution of this substance. Harmine or harmaline, by reduction in acid or alkaline solution, yields the same tetrahydroharmine as the end-

product, and up to the present no more highly hydrogenated deriv-
ative has been obtained. The reduction of metho-salts of har-
maline produces a methyltetrahydroharmine, and this is the true
N-methyl derivative of tetrahydroharmine because the latter is
converted into the methyl hydrogen sulphate of the former by
treatment with methyl sulphate (see p. 961). Evidently, the four
hydrogen atoms which may be added to harmine and some of its
derivatives always assume the same positions in the molecule, and
this is clearly due to the hydrogenation of the pyridine nucleus
leaving the indole nucleus intact. It is well known that indoles are
exceedingly difficult to reduce, and the fact that harmine yields
only a tetrahydro-derivative is to be regarded as evidence confirm-
ing our view of the nature of its fundamental structure. Tetra-
hydroharmine is shown in IX, and it is desirable at this stage to
consider whether or no a substance of this constitution would couple
with diazonium salts in the way which is so characteristic of this
base (see p. 936). It might well be thought that a dialkylindole
would not be reactive on account of the conjugation of the nitrogen
in the indole ring, and for comparison we prepared a pure speci-
men of 2:3-dimethylindole by repeated treatment of the crude
substance with *p*-dimethylaminobenzaldehyde in warm alcoholic
hydrochloric acid solution. The product was quite free from ethyl-
indole, and gave no pine-shaving reaction and no coloration with
p-dimethylaminobenzaldehyde in aqueous-alcoholic hydrochloric
acid solution. In dilute acetic acid it condensed with diazobenzene-
sulphonic acid with the production of an orange-red azo-compound.
In the case of IX there is also a methoxyl group in the ortho-posi-
tion to the point of entry of the azo-group, and this is a circum-
stance which is well known to facilitate the coupling and to enhance
the halochromic phenomena of the product. Obviously formula IX
represents a substance which should behave towards diazo-salts as
tetrahydroharmine actually does :

(IX.)

(X.)

(XI.)
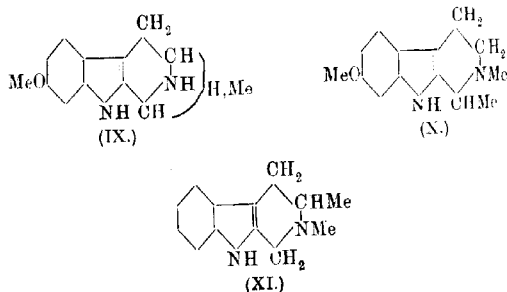
A curious analogy between tetrahydroharmine and 2 : 3-dimethyl-indole is shown by the colour reactions with p-dimethylaminobenz-aldehyde and aqueous-alcoholic hydrochloric acid on heating. The dimethylindole slowly develops a pale blue colour, which fades to pale greenish-yellow on cooling the solution, and the alternation of colours on heating and cooling can be made as often as desired. Tetrahydroharmine behaves entirely similarly except that the hot liquid is bluish-pink and the cold solution yellow.

Returning to the question of the position of the methyl group in harmine, N-methyltetrahydroharmine will be X or XI according as harmine is taken as VI or VII respectively. On oxidation with potassium permanganate in acetone solution this base, $C_{14}H_{18}ON_2$, is partly converted into a neutral substance melting at 228°, which has the composition $C_{13}H_{14}O_2N_2$, and clearly the newly acquired oxygen atom forms part of a carbonyl group which by direct union with the basic nitrogen neutralises its salt-forming character. At the same time the oxidation has removed a carbon atom, most probably originally in the form of a methyl group. This substance (m. p. 228°) was recovered unchanged after heating at 100° with phosphorus pentachloride and phosphoryl chloride, although a clear solution was obtained. On the basis of formula XI for N-methyltetra-hydroharmine, all possible structures for the oxidation product will contain either the grouping ·NH·CO· or ·CH₂·CO·, and in either case a reaction with phosphorus pentachloride would be anticipated. Assuming formula X, however, it is possible to construct two expressions (XII and XIII) for the compound (m. p. 228°), which are in harmony with its composition and other properties:

$$\begin{array}{cc} \text{(XII.)} & \text{(XIII.)} \end{array}$$
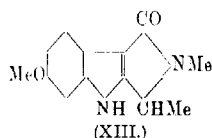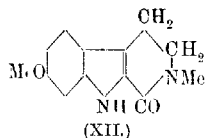
The evidence, just mentioned, is not quite conclusive, since the apparent failure to react with phosphorus pentachloride may have been due to the ready hydrolysis of the chloro-derivative by water, but, so far as it goes, it favours formula VI for harmine, and we have therefore provisionally adopted this expression. It follows that harminic acid and *apo*harmine must be represented by XIV

$$\begin{array}{cc} \text{(XIV.)} & \text{(XV.)} \end{array}$$
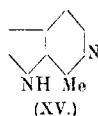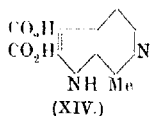
and XV respectively, and since harminic acid is no longer to be regarded as a pyridine-$\alpha\beta$-dicarboxylic acid, the elimination on heating of both carboxyl groups becomes explicable.

The Constitution of Harmaline.

Since harmaline may be oxidised to harmine (Fritzsche, *Annalen*, 1848, **64**, 365; O. Fischer, *Ber.*, 1889, **22**, 640) and reduced to tetrahydroharmine, it is to be regarded as dihydroharmine, and the most probable constitutional formulæ for the base are shown in XVI and XVII. The available evidence does not all point in one direction, but, on the balance, we favour the structure XVI as being the better summary of·the relations and properties of the base:

(XVI.)   (XVII.)
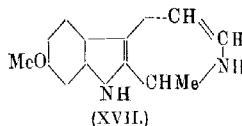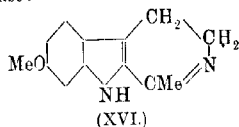
In support of the expression XVI the following considerations may be noted *inter alia*.

(1) The harmaline metho-salts, for example, the metho-chloride (see p. 952), are quaternary salts and give no precipitate on the addition of ammonia to their aqueous solutions.

(2) The fact that harmaline occurs in the seeds of *Peganum harmala* in an optically inactive condition is consistent with a formula like XVI, which contains no asymmetric carbon atom, whilst, on the other hand, a base having the constitution XVII. which implies the possibility of the existence of enantiomorphic modifications, would most probably occur in a plant in an optically active condition.

(3) Harmaline shows a tendency to form additive products, for example, with hydroxylamine (O. Fischer, *Ber.*, 1914, **47**, 105) and with hydrogen cyanide (Fritzsche, *Annalen*, 1848, **68**, 351; 1849, **72**, 307). The product of the latter process, cyanodihydroharmaline, is a base, and the whole reaction is reminiscent of that between cotarninium or hydrastinium salts and potassium cyanide. Like cyanohydrocotarnine, cyanodihydroharmaline is resolved into its components on warming with a mineral acid. The ketimino-type structure of XVI furnishes an explanation of these additive reactions.

(4) The oxidation of tetrahydroharmine with production of harmaline (see below) is more readily understood with the aid of the formula XVI than with XVII.

The more important arguments in favour of XVII are the following :

(1) Harmaline forms an acetyl derivative and an N-methyl derivative closely resembling the parent base.

(2) Harmaline condenses with diazonium salts with formation of bisazo-compounds (O. Fischer and W. Boesler, *Ber.*, 1912, **45**, 1930). On the assumption that XVII is correct, this behaviour is explicable since one point of coupling would be in the benzene ring as in the case of tetrahydroharmine, whilst the second point of attack is in the group ·CH:CH·NH·, which is contained as such or in a homologous form in many non-benzenoid substances which form azo-derivatives on treatment with diazonium salts.

(3) The possibility of migration of the ethylene linking may be held to discount to some extent the arguments 1 and 2 advanced in support of formula XVI.

A formula for harmaline must be grounded on a knowledge of the constitution of harmine, and until the position of the methyl group in the latter is known with a greater approach to certainty it is impossible to be quite sure that there is no alternative to the suggestions which have been discussed.

Harmaline forms a normal methosulphate which is readily oxidised by potassium permanganate in acetone solution (see p. 960), yielding the substance (m. p. 228°) mentioned above as the oxidation product of N-methyltetrahydroharmine. There is therefore an interdependence between the constitutions assumed for harmaline and for the substance melting at 228°. Formula XVI for harmaline corresponds with XII for the oxidation product, whilst XIII for this substance and XVII for harmaline are similarly related.

Methylharmine.

It has been tacitly assumed that the basic nitrogen of harmine is that which is contained in the pyridine nucleus, and the basis of this theory may now be more particularly stated. Harmine closely resembles carbazole in constitution, and the nitrogen atom of carbazole is almost devoid of basic character, so that the similarly situated nitrogen of the imino-group of harmine should also lack salt-forming character. This point of view is supported by the fact that harmine is similar to carbazole in the degree of reactivity of its benzene nucleus and by the correspondence in properties between tetrahydroharmine and a dialkylindole. Again, the metho-salts of harmine are quaternary salts, so that they can scarcely have been formed by addition to an imino-group, and these salts exhibit the

M M*

same fluorescence in aqueous solution as a harmine salt. Finally, *N*-acetyltetrahydroharmine is not a base.

Accordingly, if harmine is VI, harmine methosulphate (p. 951), which is typical of the harmine metho-salts, must be represented by the formula XVIII:

MeO \[\] N$<^{Me}_{SO_4Me}$

NH Me

(XVIII.)
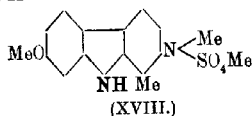
An aqueous solution of this salt gives no precipitate with ammonia or even with very dilute sodium hydroxide, but, on the addition of more sodium hydroxide, a yellow, chalky precipitate is obtained, and this appears to have the composition $C_{14}H_{14}ON_2,3H_2O$, and is probably the quaternary ammonium hydroxide corresponding with XVIII with two molecules of water of crystallisation. By heating at 100° this hydrated material is changed into methyl-harmine melting at 209° (compare O. Fischer, *Ber.*, 1897, **30**, 2482). The salts of this substance with acids are identical with the corre-sponding metho-salts of harmine, and it is reconverted into the ammonium hydroxide by boiling with water. There are three possible ways of representing the elimination of water from harmine methohydroxide with the formation of methyl harmine. In the first place a group, :N:CH$_2$, might be formed, but this would result in an unusual type of quinquevalent nitrogen, and if this were the true explanation the loss of water from methylpyridinium hydr-oxides and methylquinolinium hydroxides with the formation of methylpyridines and methylquinolines might be anticipated. The second view might be that the C-methyl group is involved, ·C(CH$_3$):NMe(OH)·, being changed into ·C(:CH$_2$)·NMe·. This possibility is excluded by the observation (p. 951) that norharmine methosulphate on decomposition with hot aqueous sodium hydr-oxide yields a methylnorharmine entirely resembling methylhar-mine. The third and only remaining alternative quite free from objection is that water is eliminated by the combination of the hydroxyl of the quaternary ammonium hydroxide and the hydrogen of the imino-group in the pyrrole nucleus. This leads to the formulæ XIX and XX for methylnorharmine and methylharmine respectively:

MeO \[\] NMe   MeO \[\] NMe

N   N   Me

(XIX.)   (XX.)
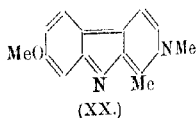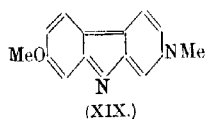
These formulæ are based on a conception of the nature of aromatic types which is comparable to that expressed in the Kekulé benzene formula, and it is on this account that the arrangement of the valencies appears somewhat unusual and the close relation with harmine is obscured. If, however, the symbols
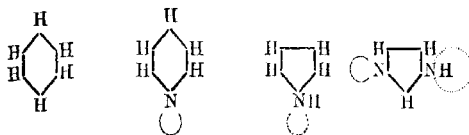
are employed for benzene, pyridine, pyrrole, and glyoxaline respectively, the corresponding expressions for harmine and methylharmine are **XXI** and **XXII**, and it will be seen that the difference between the ring-systems is almost confined to the function of the nitrogen atoms. The thickened lines in all these formulæ represent a sesqui-valency and the dotted loops attached to the nitrogen atoms indicate that a partial use for nuclear conjugation has been made of the latent valencies.


(XXI.)　　　　　　　(XXII.)
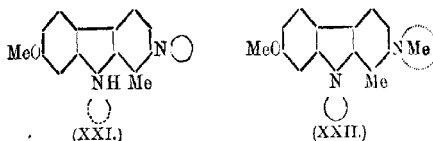
On gently warming with sulphuric acid, methylharmine is sulphonated and an extremely sparingly soluble, colourless substance, $C_{11}H_{14}O_4N_2S$, is precipitated on the addition of water. In view of the fact that methylharmine may be regenerated by prolonged boiling with dilute hydrochloric acid, this compound may be the anhydride of harmine methohydroxide N-sulphonic acid. A similar pale yellow, sparingly soluble substance, $C_{11}H_{16}O_4N_2S$, is obtained by warming harmaline methochloride with concentrated sulphuric acid and pouring the solution into water. The sulphonic group may also be in the benzene nucleus, and the matter is being further investigated.

The Synthesis of Harmine and Harmaline in the Plant.

One of the strongest arguments in favour of the main outlines of the views which have been developed above is that, unlike the older formulæ, the new expressions contain a ring-system which is related to that of an important and widely distributed amino-acid, namely, tryptophan. The actual starting point is, however, not

M M 2*

showed the presence of two methoxyl groups, so that the additional
carbon atom is most probably derived from the methyl alcohol used
as solvent, and this was confirmed by the fact that when ethyl-
alcoholic potassium hydroxide was employed in the reaction a new
substance, $C_{17}H_{26}O_2N_2$, was obtained. Unfortunately, the latter
compound could not be crystallised, but the analytical results were
sufficiently satisfactory to establish the point at issue. The base
(m. p. 129°) is produced in our view in accordance with the follow-
ing scheme:
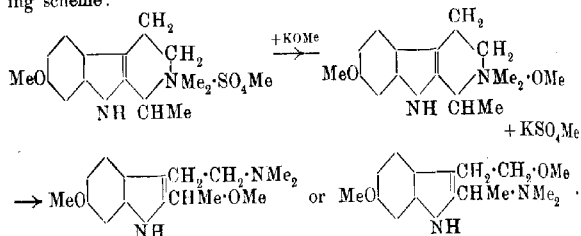
The fact that ethers of this kind are readily formed has been
demonstrated by M. Scholtz (*Ber.*, 1913, **46**, 2138), who found that
aldehydes react with 2-methylindole in alcoholic solution in the
presence of sodium hydroxide with the formation of substances of
the type

$$OEt \cdot CHR \cdot C \diamondsuit^{C_6H_4}_{CMe} > NH.$$
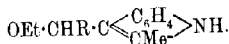
EXPERIMENTAL. .

Harmine Metho-salts.

Harmine Methosulphate, $C_{13}H_{12}ON_2, Me_2SO_4$.—This derivative is
readily prepared by rubbing harmine (1 gram) into a paste with
methyl sulphate (1 c.c.), leaving for twenty-four hours, and then
dissolving the solid product in boiling methyl alcohol. On cooling,
the methosulphate separates as a pale yellowish-green, crystalline
mass, and, after repeated recrystallisation, is obtained almost
colourless. In preparing larger quantities, a good plan is to cover
the finely powdered harmine with benzene, and, after adding the
methyl sulphate, to heat on the steam-bath, when combination takes
place rapidly and is complete in half an hour. The product is
washed with benzene by the aid of the pump and drained on porous
porcelain. A specimen, which had been crystallised from water
and left exposed to the air until dry, yielded the following analyti-
cal results:

0·1288 lost 0·112 at 100°. $H_2O = 8·7$.

*0·1176 gave 0·2316 CO_2 and 0·0580 H_2O. C = 53·7 ; H = 5·3.

$C_{13}H_{12}ON_2, Me_2SO_4, 2H_2O$ contains $H_2O = 9·6$ per cent. and

$C_{13}H_{12}ON_2, Me_2SO_4$ requires C = 53·3 ; H = 5·3 per cent.

Harmine methosulphate melts at about 220° and is readily soluble in hot water, from which it separates as a voluminous mass of needles; it is also readily soluble in boiling methyl alcohol, but much less so in the cold. The aqueous solution is not precipitated by ammonia, but sodium hydroxide gives at once a voluminous, yellow, crystalline precipitate of the hydrated ammonium hydroxide (see p. 948).

Harmine Methiodide, $C_{13}H_{12}ON_2, MeI.$—This substance, first prepared by O. Fischer and E. Taüber (*Ber.*, 1885, **18**, 402) by the direct addition of methyl iodide to harmine, is conveniently obtained in the following manner. Harmine methosulphate (5 grams) dissolved in boiling water (150 c.c.) is mixed with boiling dilute potassium iodide (5 grams), when an immediate voluminous, almost colourless precipitate separates; this is collected and crystallised from alcohol, from which it separates in needles. When rapidly heated it darkens at 290° and melts at 305—307° to a black mass.

Harmine Methochloride, $C_{13}H_{12}ON_2, MeCl.$—This characteristic derivative is obtained when harmine methiodide, ground into a paste with much hot water, is digested on the steam-bath with a considerable excess of freshly prepared silver chloride. After filtering, the nearly colourless filtrate is concentrated and left overnight, when the liquid becomes filled with a mass of very pale yellow needles which exhibit a slight green fluorescence. The air-dry substance gave the following. analytical results:

1·4307, heated at 100°, lost 0·2769. $H_2O = 19·4$,

*0·1234 gave 0·2905 CO_2 and 0·0631 H_2O. C = 64·2 ; H = 5·7.

$C_{13}H_{12}ON_2, MeCl, 4H_2O$ contains $H_2O = 21·5$ and $C_{13}H_{12}ON_2, MeCl$
    requires C = 64·0 ; H = 5·7 per cent.

Harmine methochloride, when rapidly heated, scarcely darkens at 280° and melts at about 305° with effervescence to a black froth; it is rather sparingly soluble in boiling methyl alcohol and separates well in colourless groups of slender, prismatic needles. Its aqueous solution fluoresces blue and resembles the methosulphate in its behaviour with ammonia and sodium hydroxide.

Methylharmine (Formula XX or XXII).

This substance, first prepared by O. Fischer (*Ber.*, 1897, **30**, 2482) from harmine methiodide by treatment with potassium hydr-

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* Dried at 100°.

oxide, is described as a colourless substance which melts at 209°, crystallises from benzene in needles, and rapidly absorbs carbon dioxide from the air. We have prepared methylharmine from harmine methosulphate and methochloride by the action of sodium hydroxide. The aqueous solution of either of these derivatives gives a voluminous, yellow precipitate on the addition of sodium hydroxide in the cold, and this is readily soluble in hot water and separates, on cooling slowly, in long, very pale yellow needles. After twice crystallising from water, the substance was left for three days exposed to the air and then analysed :

I. 1·1407, heated at 100°, lost 0·1999. $H_2O = 17·5$.

0·1033 gave 0·2350 CO_2 and 0·0668 H_2O. C = 62·0 ; H = 7·2.

$C_{14}H_{14}ON_2,3H_2O$ requires $H_2O = 19·3$; C = 60·0 ; H = 7·1 per cent.

II. Two specimens, heated at 100° until constant, gave the following analytical results :

0·1172 gave 0·3181 CO_2 and 0·0649 H_2O. C = 74·0 ; H = 6·2.

0·1286 ,, 0·3506 CO_2 ,, 0·0715 H_2O. C = 74·3 ; H = 6·3.

$C_{14}H_{14}ON_2$ requires C = 74·3 ; H = 6·2 per cent.

It is clear that the substance precipitated from harmine methosulphate or methochloride by sodium hydroxide is a hydrate of the probable composition, $C_{14}H_{14}ON_2,3H_2O$, and that this loses all its water at 100°, leaving pure methylharmine which, as stated by Fischer, melts at 209°. The following experiment supports the view that the hydrate crystallised from water is harmine methohydroxide with $2H_2O$. When the hydrate is exposed over sulphuric acid in a vacuum desiccator it rapidly loses $2H_2O$ and the last H_2O with much greater difficulty. Thus a specimen which had been exposed in the desiccator for six hours yielded C = 69·0 ; H = 6·7 ; after twenty-four hours it contained C = 70·8 ; H = 6·4, and after two days C = 71·5 ; H = 6·2, whereas $C_{14}H_{14}ON_2,H_2O$ requires C = 68·8 ; H = 6·4 per cent.

Exposure to the air did not in our experience lead to the formation of carbonate as suggested by O. Fischer, since, after seven days' exposure, there was no effervescence on the addition of hydrochloric acid. Also analytical results are recorded above for air-dried material, and these were apparently not vitiated by absorption of carbon dioxide. *Methylharmine hydrochloride* is obtained as a sparingly soluble precipitate when the above hydrate is mixed with dilute hydrochloric acid. It crystallises from boiling dilute hydrochloric acid as a voluminous mass of needles, melts and decomposes at 305°, and is identical with harmine methochloride. (Found. C = 64·1 ; H = 5·8. $C_{14}H_{14}ON_2,HCl$ requires C = 64·0 ; H = 5·7 per cent.)

Methylharmine Methosulphate, $C_{14}H_{14}ON_2,Me_2SO_4$.—Methylharmine reacts with methyl sulphate with the evolution of much heat and, in preparing the methosulphate, it is necessary either to employ small quantities of material or to use a diluent, such as benzene. When methylharmine (1 gram) is rubbed with methyl sulphate (1 c.c.), a stiff, chalky paste is soon formed and, after remaining overnight, the product is recrystallised from methyl alcohol, in which the methosulphate is unusually sparingly soluble and from which it separates as a voluminous mass of colourless needles:

0·1107 gave 0·2221 CO_2 and 0·0580 H_2O. C = 54·7; H = 5·8.
$C_{14}H_{14}ON_2,Me_2SO_4$ requires C = 54·6; H = 5·7 per cent.

Methylharmine methosulphate is readily soluble in water and both the aqueous and methyl-alcoholic solutions, especially when dilute, exhibit a beautiful, pure blue fluorescence. It separates from a concentrated aqueous solution in felted needles. The solution in acetic acid gives, on the addition of sulphuric acid, a yellow liquid with a striking green fluorescence reminiscent of that of alkaline fluorescein; after a time the yellow colour and the fluorescence disappear, and the addition of a drop of dilute nitric acid produces a reddish-violet coloration. In concentrated sulphuric acid a similar fluorescent solution is obtained, and, on gently warming, this very rapidly fades and a colourless solution with violet fluorescence results. On the addition of water an extremely sparingly soluble precipitate consisting of colourless, satiny needles is formed. This substance contains sulphur, but differs from the sulphonic derivatives described on pp. 950, 953 in not being affected by aqueous sodium hydroxide even on boiling. The aqueous solution of the methosulphate is coloured yellow by potassium hydroxide, and, on heating to boiling, the yellow colour disappears, and if cooled much of the methosulphate separates unchanged. If, however, the boiling is continued for some time, a substance separates on cooling which appears to be the corresponding ammonium hydroxide. This was collected and dissolved in a large excess of boiling dilute hydrochloric acid, from which *methylharmine methochloride,* $C_{14}H_{14}ON_2,MeCl$, separated as a voluminous mass of colourless needles:

0·1108 gave 0·2631 CO_2 and 0·0615 H_2O. C = 64·8; H = 6·2.
$C_{14}H_{14}ON_2,MeCl$ requires C = 65·1; H = 6·7 per cent.

This methochloride becomes yellow at 270° and melts at about 280—285° with effervescence to a reddish-brown syrup. The aqueous solution exhibits a fine blue fluorescence and becomes yellow on the addition of ammonia or sodium hydroxide, but no precipitate sepa-

rates. When, however, the aqueous solution, rendered strongly alkaline by sodium hydroxide, is boiled and concentrated, it deposits a pale yellow, crystalline precipitate, which dissolves in dilute hydrochloric acid with regeneration of the methochloride.

Harmine Methohydroxide Sulphonic Anhydride,

$$MeO \overbrace{\qquad} N Me \quad (?)$$
$$N \quad Me$$
$$SO_2 \!\!—\!\! O$$
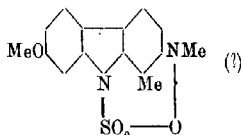
On one occasion, in preparing harmine methosulphate at 100° in an open vessel, it was noticed that instead of the expected product a very sparingly soluble, colourless substance was formed, and this result was traced to hydrolysis of the methyl sulphate and formation of sulphuric acid, which even under these conditions readily sulphonated the harmine methosulphate. It was then found that the same substance could be obtained by treating methylharmine in acetic anhydride with a few drops of sulphuric acid and by warming harmine methosulphate with concentrated sulphuric acid. A theoretical yield was obtained in the following manner. Harmine (5 grams) was finely powdered and heated during an hour on the steam-bath with toluene (20 c.c.) and methyl sulphate (15 c.c.), concentrated sulphuric acid (10 c.c.) was then added and the heating continued during half an hour. After the addition of water the precipitate was collected and dissolved in dilute sodium hydroxide. The filtered solution was diluted to 2000 c.c., heated to boiling, and acidified by the addition of hydrochloric acid. Almost immediately the substance crystallised from the solution in colourless, microscopic needles, which were collected, washed with hot water, and dried at 100° :

0·1301 gave 0·2629 CO_2 and 0·0545 H_2O. $C = 55·1$; $H = 4·7$.

0·1272 ,,   0·0958 $BaSO_4$. $S = 10·3$.

$C_{14}H_{14}O_4N_2S$ requires $C = 54·9$; $H = 4·6$; $S = 10·5$ per cent.

This compound is very sparingly soluble in organic solvents and in water. It dissolves to some extent in boiling dilute hydrochloric acid and separates on cooling in an unchanged condition. Its solution in concentrated sulphuric acid is colourless, and exhibits a bluish-violet fluorescence. It is readily soluble in aqueous sodium hydroxide to a yellow solution, from which acids precipitate the original substance, but it is not attacked by cold sodium carbonate. A small quantity was boiled with dilute hydrochloric acid during

fourteen successive working days, when it was noticed that the .
amount which had separated, on cooling overnight, became smaller
and smaller. On the addition of sodium hydroxide a precipitate
was obtained, and this was collected and crystallised from benzene,
when pale yellow needles of methylharmine melting at 209° were
obtained. It is also possible to hydrolyse the substance with the
formation of harmine. It slowly dissolved in boiling glycerol, and
on pouring the solution into water only a small amount of insoluble
material remained in suspension. The filtered liquid was mixed
with sodium hydroxide, the precipitate collected and crystallised
from alcohol. The colourless needles so obtained melted at 256°
alone or when mixed with a specimen of pure harmine.

Methylnorharmine (Formula XIX).

Norharmine (2 grams) (Perkin and Robinson, T., 1912, **101**,
1786) was dissolved in the minimum quantity of boiling benzene
and methyl sulphate (5 c.c.) added to the solution, which was not
again heated. The methosulphate soon separated as an oil, which
later crystallised, and after leaving overnight the benzene was
decanted and the solid washed with ether and then dissolved in
water. The colourless solution exhibited blue fluorescence, and on
the addition of an excess of sodium hydroxide a yellow, chalky
precipitate was obtained. This was collected, dried in a vacuum
desiccator over phosphoric oxide, and crystallised from dry benzene.
The very pale yellow, flat needles melted at 195—196° with slight
previous softening:

0.1049 gave 0.2832 CO_2 and 0.0549 H_2O. $C = 73.6$; $H = 5.8$.

$C_{13}H_{12}ON_2$ requires $C = 73.6$; $H = 5.7$ per cent.

Methylnorharmine is moderately readily soluble in alcohol, but
sparingly so in benzene; it also dissolves in boiling water and crys-
tallises on cooling, probably as norharmine methohydroxide. It has
a great superficial resemblance to methylharmine, and dissolves in
sulphuric acid to a similar yellow solution with bright green fluores-
cence. Its solutions in dilute aqueous acids exhibit a blue
fluorescence.

Harmaline Metho-salts.

Harmaline Methosulphate, $C_{13}H_{14}ON_2,Me_2SO_4$.—Harmaline com-
bines more energetically with methyl sulphate than does harmine,
and the methosulphate is readily prepared by rubbing harmaline
(1 gram) with methyl sulphate (1 c.c.), when, even with such small
quantities, a considerable rise of temperature will be observed.

After a few hours the yellow mass is crystallised from methyl alcohol, from which the methosulphate separates in yellow needles, and the mother liquor, on the addition of ether, gives a further crop of the same substance. Larger quantities are best prepared, in almost quantitative yield, under the following conditions. Finely powdered and sieved harmaline (30 grams) is covered with benzene (50 c.c.) and mixed with methyl sulphate (30 c.c.), when there is no immediate development of heat, but, on keeping, the temperature gradually rises to about 40°. After remaining for two days, the crystalline mass is collected, washed with benzene, and drained on porous porcelain ; it is then pure enough for many purposes :

0·4332 gave 0·2989 BaSO$_4$. S = 9·4.

$C_{13}H_{14}ON_2,Me_2SO_4$ requires S = 9·4 per cent.

Harmaline methosulphate shrinks at 160° and melts at about 170—172° to a deep yellow liquid ; it is readily soluble in water or alcohol. The addition of sodium hydroxide to the cold concentrated aqueous solution gives a viscid, orange-red precipitate which, when washed free from alkali and boiled with water, becomes yellow and crystalline, and this substance appears to be nearly pure methylharmaline (compare O. Fischer, *Ber.*, 1897, **30**, 2484 ; 1914, **47**, 102). The boiling aqueous solution of the methosulphate gives, on the addition of potassium iodide, an immediate yellow, crystalline precipitate of the methiodide, $C_{13}H_{14}ON_2,MeI$. This method of preparation yields at once the pure methiodide, and is therefore to be preferred to the direct combination of harmaline with methyl iodide, since by this latter process dimethylharmaline iodide is also produced (O. Fischer, *Ber.*, 1914, **47**, 104).

Harmaline Methochloride, $C_{13}H_{14}ON_2,MeCl,4H_2O$.—This substance is readily prepared by digesting a paste of harmaline methiodide and much water with an excess of silver chloride on the steam-bath for a couple of hours and filtering. The filtrate is concentrated and allowed to cool slowly, when the methochloride separates as a crust of pale yellow, glistening prisms with a faint green lustre :

*1·0380 lost 0·2223 in the steam-oven. H$_2$O = 21·6.

†0·1323 gave 0·3097 CO$_2$ and 0·0786 H$_2$O. C = 63·9 ; H = 6·6.

$C_{13}H_{14}ON_2,MeCl,4H_2O$ contains H$_2$O = 21·4 and $C_{13}H_{14}ON_2,MeCl$ requires C = 63·5 ; H = 6·4 per cent.

Harmaline methochloride begins to decompose at 260° and melts at about 278° with vigorous effervescence to a reddish-brown froth. It is very readily soluble in hot water or acetic acid, sparingly so in alcohol, and almost insoluble in boiling acetone. The aqueous

* Air-dry.   † Dried at 100°.

solution is not precipitated by ammonia, and the bearing of this observation on the constitution of harmaline has been referred to on p. 940. Sodium hydroxide decomposes the salt in aqueous solution and produces an orange-red, viscid mass, which, when washed and boiled with water, becomes yellow and crystalline and doubtless consists of methylharmaline (see above).

The cold aqueous solution of the methochloride instantly decolorises permanganate.

Harmaline Methohydroxide Sulphonic Anhydride,
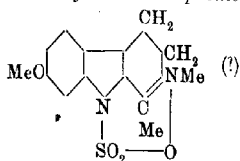
When finely divided harmaline methochloride is mixed with concentrated sulphuric acid, it dissolves to an orange-red solution with vigorous evolution of hydrogen chloride. If, after heating on the steam-bath for five minutes, water is added, a substance gradually separates as a voluminous mass of pale lemon-yellow needles. The compound is extremely sparingly soluble in water, but may be crystallised from much boiling water and obtained in long, lemon-yellow needles which become opaque and chalky in the steam-oven. It contains sulphur:

0·1050 gave 0·2108 CO_2 and 0·0494 H_2O. $C = 54·7$; $H = 5·2$.

$C_{14}H_{16}O_4N_2S$ requires $C = 54·5$; $H = 5·2$ per cent.

This substance is almost insoluble even in boiling acetic acid, it does not melt and scarcely shows any sign of decomposition at 300°. It is not soluble in cold aqueous sodium carbonate, but dissolves on the addition of a drop of sodium hydroxide to a yellow solution, and is precipitated unchanged by hydrochloric acid.

Reduction of Harmaline Methosulphate or the Methochloride:

Formation of Methyltetrahydroharmine.

In the first of these reductions, harmaline methosulphate (3 grams), dissolved in dilute sulphuric acid, was reduced in a porcelain beaker fitted with a mechanical stirrer with 3 per cent. sodium amalgam (200 grams), when the colour of the solution gradually faded and the process was completed by heating on the steam-bath. The filtered liquid, rendered alkaline by the addition

of sodium hydroxide, yielded a gummy mass, which soon hardened, and the solution in boiling methyl alcohol deposited, on cooling and stirring vigorously, a mass of glistening plates which, after recrys-tallisation, melted at 174—176°. This substance has the formula $C_{14}H_{18}ON_2$ (Found, $C = 72\cdot8$; $H = 8\cdot0$; $N = 12\cdot1$. $C_{14}H_{18}ON_2$ requires $C = 73\cdot1$; $H = 7\cdot8$; $N = 12\cdot2$ per cent.), and is evidently identical with the methyldihydroharmaline which O. Fischer (*Ber.*, 1914, **47**, 103) obtained from methylharmaline hydrochloride by reducing in amyl-alcoholic solution with sodium. In the second experiment, which appears to give the purer product, harmaline methochloride (5 grams), dissolved in water (300 c.c.) and hydro-chloric acid (50 c.c.), was reduced on the steam-bath by the rapid addition of 3 per cent. sodium amalgam (250 grams). The yellow colour of the methochloride solution rapidly disappeared, and, on adding sodium hydroxide and crystallising the solid base from methyl alcohol, a crust of colourless prisms of methyltetrahydro-harmine was obtained which melted directly at 176°.

Methyltetrahydroharmine Methosulphate, $C_{14}H_{18}ON_2,Me_2SO_4$.—When methyltetrahydroharmine (2 grams) is mixed with methyl sulphate (3 c.c.) it dissolves with considerable rise of temperature and the clear syrup suddenly crystallises. A rather better yield is obtained if the base is covered with benzene before mixing with methyl sulphate (see p. 946), when a syrup separates which rapidly crystallises.

The product is then recrystallised from methyl alcohol, in which it is readily soluble and from which it separates as a hard crust of well-developed, colourless prisms * :

$0\cdot1049$ gave $0\cdot2054$ CO_2 and $0\cdot0655$ H_2O. $C = 53\cdot4$; $H = 6\cdot9$.
$0\cdot1181$,, $0\cdot2327$ CO_2 ,, $0\cdot0688$ H_2O. $C = 53\cdot7$; $H = 6\cdot5$.
        $C_{16}H_{24}O_5N_2S$ requires $C = 54\cdot0$; $H = 6\cdot7$ per cent.

This methosulphate melts at about 188° without effervescence and is readily soluble in water, yielding a solution which has an extremely bitter taste.

Crystals of methyltetrahydroharmine methosulphate were kindly examined by Miss M. W. Porter, who finds that they are mono-clinic with $a : b = 0\cdot738$, $\beta = 96°55'$. The crystals are of a stout,

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* A considerable amount of methosulphate remains in the mother liquors and, if the methyl alcohol is removed by distillation from the steam-bath, most of this decomposes and is converted into a tar.

The best plan is to expose the mother liquor over sulphuric acid in a vacuum desiccator, when a hard crust gradually separates mixed with some tar; the latter can be removed by rubbing with cold methyl alcohol and leaving in contact with porous porcelain.

prismatic habit, as shown in Fig. 1, and exhibit the forms $b(010)$, $m(110)$, and $c(001)$. The faces were somewhat curved. Following are the means of the two angles measured: m(azimuth) = $53°47'$, c(polar distance) = $6°55'$.

FIG. 1.

isoMethyltetrahydroharmine Methohydroxide Methyl Ether,

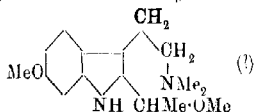$$\text{MeO} \underset{\text{NH}}{\overset{\text{CH}_2}{\bigodot}} \overset{\text{CH}_2}{\underset{\text{CHMe·OMe}}{\bigl| \, \text{NMe}_2\bigr|}} \quad (?)$$
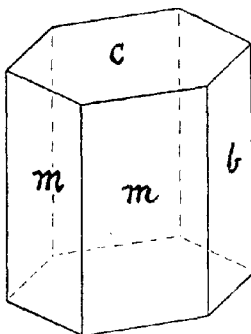
This substance, which is evidently identical with that obtained by O. Fischer (*Ber.*, 1914, **47**, 104) from the product of the action of methyl iodide on methyltetrahydroharmine by decomposition with methyl-alcoholic potassium hydroxide (compare p. 946), is readily prepared in the following manner: Methyltetrahydroharmine methosulphate (1 gram), dissolved in a little boiling methyl alcohol, is mixed with methyl-alcoholic potassium hydroxide (10 c.c. of 25 per cent.) and boiled for half an hour. Most of the methyl alcohol is then evaporated under reduced pressure and water added, when an oil separates which soon crystallises. The substance is readily purified by recrystallisation from ether, when it separates as a mass of colourless needles or from a mixture of benzene and light petroleum, from which it crystallises in flat needles. In view of the fact that this substance appeared to have a composition different from that $(C_{15}H_{22}O_2N_2)$ assigned to it by O. Fischer (*loc. cit.*, compare p. 945), it became necessary to carry out several analyses. The following were made with three different preparations, the first

two having been twice recrystallised from ether and the third from benzene and light petroleum in addition:

I. 0.1067 gave 0.2733 CO_2 and 0.0840 H_2O. $C = 69.8$; $H = 8.7$
   0.2093 ,, 18.7 c.c. N_2 at $11.5°$ and 732 mm. $N = 10.2$.

II. 0.1059 ,, 0.2705 CO_2 and 0.0829 H_2O. $C = 69.7$; $H = 8.7$.

III. 0.1214 ,, 0.3102 CO_2 ,, 0.0953 H_2O. $C = 69.7$; $H = 8.7$.

$C_{16}H_{24}O_2N_2$ requires $C = 69.6$; $H = 8.7$; $N = 10.1$ per cent.

$C_{15}H_{22}O_2N_2$,, $C = 68.7$; $H = 8.4$; $N = 10.7$,,   · ,,

The analytical results given by O. Fischer are $C = 69.1$ and 69.0; $H = 8.78$ and 8.67; and $N = 10.81$.

A methoxyl determination by Zeisel's method yielded the following result:

0.2865 gave 0.4790 AgI. MeO $= 22.1$.

$C_{16}H_{24}O_2N_2$, containing 2MeO, requires MeO $= 22.4$ per cent.

iso*Methyltetrahydroharmine methohydroxide methyl ether* melts at 128—129° and is readily soluble in alcohol, acetone, or benzene, but sparingly so in water, ether, or light petroleum. It crystallises from dilute methyl alcohol in large, colourless plates or from much light petroleum in groups of flat needles. When it is heated in small quantities it distils with only slight decomposition, but, under 10 mm. pressure, it passes over without residue as a colourless syrup which, when rubbed, solidifies completely. After washing with ether on porous porcelain, the colourless, crystalline mass melted at 121—126° and the admixture with the original substance at 123—126°, showing that no change, such as elimination of water, had taken place during the distillation.

iso*Methyltetrahydroharmine Methohydroxide Ethyl Ether*, $C_{17}H_{26}O_2N_2$.—In order to confirm the composition given for the product of the action of methyl alcohol on methyltetrahydroharmine methosulphate, the latter substance (1 gram) was digested with ethyl-alcoholic potassium hydroxide (10 c.c. of 20 per cent.) for an hour. On adding water, a viscid, ochreous precipitate separated, which was extracted with ether, and the ethereal solution, after thoroughly washing and drying over potassium carbonate, concentrated and left in the ice-chest for a week, but nothing separated.

The ether was then allowed to evaporate slowly over sulphuric acid, when a pasty mass of crystals remained, which was left in contact with porous porcelain until quite dry and hard. As all attempts to recrystallise this substance were unsuccessful, it was dried over phosphoric oxide and analysed:

0.1399 gave 0.3614 CO_2 and 0.1116 H_2O. $C = 70.4$; $H = 8.8$.

$C_{17}H_{26}O_2N_2$ requires $C = 70.3$; $H = 9.0$ per cent.

When treated with hydrochloric acid and then with potassium iodide, this substance yields a hydrochloride, $C_{15}H_{20}ON_2,HCl$, and hydriodide, $C_{15}H_{20}ON_2,HI$ (m. p. 290—295°), identical with those produced under the same conditions from *iso*methyltetrahydroharmine methohydroxide methyl ether (see below).

Dehydroisomethyltetrahydroharmine Methohydroxide,

, (?) *or its Polymeride*.
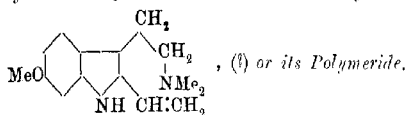
The *hydrochloride*, $C_{15}H_{20}ON_2,HCl$, of this base is obtained when *iso*methyltetrahydroharmine methohydroxide methyl ether is treated with dilute hydrochloric acid. The methyl ether dissolves in cold dilute hydrochloric acid, and almost immediately the solution clouds and a caseous substance separates, which soon hardens. This curious salt melts under hot water, dissolves to a pale violet solution, and the addition of hydrochloric acid causes a very pale blue, apparently crystalline, precipitate to separate, which was collected, washed with dilute hydrochloric acid, and dried on porous porcelain over solid potassium hydroxide and then in the steam-oven:

0·1032 gave 0·2415 CO_2 and 0·0707 H_2O.   C = 63·8; H = 7·6.

$C_{15}H_{20}ON_2,HCl$ requires C = 64·2; H = 7·5 per cent.

This hydrochloride is readily soluble in water, but sparingly so in dilute hydrochloric acid; the aqueous solution gives on the addition of platinic chloride a pale brown precipitate, which on warming becomes black, and with auric chloride a drab precipitate which becomes violet on heating owing to the separation of metallic gold. When ammonia is added to the solution of the hydrochloride a nearly colourless jelly separates, which is evidently the free dehydro-base (see below).

The *Hydriodide*, $C_{15}H_{20}ON_2,HI$.—The methyl ether dissolves in dilute sulphuric acid at 40°, and, on keeping, the solution clouds and deposits a caseous precipitate of the sulphate, which gradually becomes crystalline.

This was collected, dissolved in warm water, and mixed with potassium iodide, when a sparingly soluble, amorphous precipitate separated, which also became crystalline on warming. After washing well and drying in the steam-oven, this hydriodide was analysed:

0·1089 gave 0·1954 CO_2 and 0·0567 H_2O.   C=49·0; H=5·8.

$C_{15}H_{20}ON_2,HI$ requires C=48·7; H=5·6 per cent.

On heating in a capillary tube this iodide remains nearly colour-less until 250°, then gradually becomes brown, and melts at about 290—295° with vigorous decomposition to a black froth.

Dehydroisomethyltetrahydroharmine methohydroxide was obtained by rubbing the hydriodide to a fine paste with a large excess of dilute ammonia, and, after remaining overnight, the ochreous precipitate was collected and digested at about 60° with a further quantity of dilute ammonia, the process being repeated until no more iodine was removed. The pale ochreous precipitate was collected, thoroughly washed with dilute ammonia, and dried first in a desiccator over phosphoric oxide and then in the steam-oven:

0·1184 gave 0·3182 CO_2 and 0·0874 H_2O.   C=73·3; H=8·2.

$C_{15}H_{20}ON_2$ requires C=73·8; H=8·2 per cent.

This curious substance does not melt, and indeed scarcely darkens, at 300°; it dissolves very readily in methyl alcohol, and is precipitated as a pale ochreous precipitate on the addition of ether, but it has not so far been possible to obtain it in a definitely crystalline condition.

Boiling with dilute hydrochloric acid converts it into a sparingly soluble hydrochloride; it dissolves, however, readily in warm glacial acetic acid, yielding a colourless solution which is not precipitated by water. On the addition of ammonia, a colloidal solution is obtained which, on boiling, deposits a flocculent, gelatinous precipitate consisting apparently of the dehydro-base.

The *Methosulphate* and the *Methiodide*, $C_{15}H_{20}ON_2,MeI$.—The solution of *iso*methyltetrahydroharmine methohydroxide methyl ether (1 gram) in benzene (5 c.c.) gives, on the addition of methyl sulphate (1 c.c.), a cloudy liquid : there is considerable development of heat, and a gum separates which is evidently the methosulphate of the dehydro-base. The benzene was decanted, the gum washed with ether, dissolved in hot water and mixed with potassium iodide, when a jelly separated which, on warming, became granular :

0·1147 gave 0·2097 CO_2 and 0·0601 H_2O.   C=49·9; H=5·8.

$C_{15}H_{20}ON_2,MeI$ requires C=49·8; H=5·9 per cent.

This methiodide does not darken until 260°, and melts at about 290—292° with effervescence to a black froth.

The methosulphate behaves in a remarkable manner when its solution in methyl alcohol is boiled with methyl-alcoholic potassium hydroxide.

Trimethylamine is eliminated but with difficulty, and, on adding water, a milky liquid is produced which gradually deposits a con-

siderable rather viscid precipitate. This was collected and found to be almost insoluble in the usual organic solvents and, after it had been boiled with methyl alcohol, ether, benzene, and finally acetone, a grey mass remained which was exactly similar to india-rubber in appearance and many if its properties.

It was resilient like rubber, frothed up on heating to a high temperature, and was quite insoluble in acetic or dilute hydrochloric acid.

There can be little doubt that this mass is a polymeric modification of the divinyl derivative:
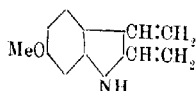
but the substance was not further investigated.

Oxidation of Methyltetrahydroharmine and of Harmaline Metho-sulphate: Formation of Ketoisonormethyltetrahydroharmine,
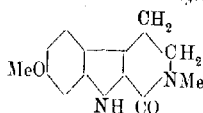
In studying the oxidation of methyltetrahydroharmine, the base (5 grams), dissolved in acetone (250 c.c.), was gradually treated with very finely powdered permanganate (11 grams) at −10°. When the decolorisation of the permanganate, which took place very slowly, was complete the product was filtered, the manganese precipitate thoroughly washed with acetone (*A*), extracted with boiling water, and the dark brown extract concentrated. On neutralising with acetic acid, precipitating with lead acetate, and decomposing the small amount of lead salt with hydrogen sulphide, only 0·5 gram of a dark, resinous acid was obtained, from which nothing crystalline could be isolated. The acetone filtrate (*A*) was concentrated considerably and allowed to remain in the ice-chest, when a heavy, crystalline precipitate rapidly separated, which was collected and washed with methyl alcohol, in which it is almost insoluble.

The substance dissolves in much boiling acetone and separates, on cooling, in glistening, pale lemon-yellow needles:

0·1012 gave 0·2498 CO_2 and 0·0555 H_2O.   C = 67·3 H = 6·1.
0·1113 ,, 0·2769 CO_2 ,, 0·0619 H_2O.   C = 67·8; H = 6·1.
$C_{13}H_{14}O_2N_2$ requires C = 67·8; H = 6·1 per cent.

*Keto*iso*normethyltetrahydroharmine* melts at 228° and is spar-
ingly soluble in the usual organic solvents. It does not dissolve in
dilute mineral acids, and its solution in glacial acetic acid is pre-
cipitated by water. Concentrated sulphuric acid dissolves the sub-
stance readily to a yellowish-brown solution, but, even after heating
on the steam-bath for some minutes, water precipitates much un-
changed substance. It is insoluble in cold concentrated hydro-
chloric acid, but when boiled with the acid it partly dissolves and a
crystalline substance separates, which appears to be the hydro-
chloride and is immediately dissociated on the addition of water.
It is also insoluble in aqueous alkalis and in cold methyl-alcoholic
potassium hydroxide, but it dissolves in the latter on boiling and
crystallises unchanged when the solution is cooled.

*Behaviour of Keto*iso*normethyltetrahydroharmine with Phos-
phoryl Chloride and Pentachloride.*—That this substance is not
readily attacked by these reagents is shown by the following experi-
ment.

When the substance (1 gram) is warmed with phosphoryl
chloride (1·5) it is converted into a voluminous, yellow mass con-
sisting probably of the hydrochloride, and if powdered phosphorus
pentachloride is now added and the whole heated on the steam-bath
a clear liquid is produced.

After heating for fifteen minutes the yellow liquid was poured on
powdered ice, when a deep orange, viscid precipitate separated,
which was collected, drained on porous porcelain, and rubbed with
cold methyl alcohol.

This removes the viscid impurity and leaves a pale ochreous
powder, which, after contact with porous porcelain and again wash-
ing with methyl alcohol, weighed 0·6 gram, melted at 225—228°,
and consisted of unchanged substance.

If the experiment is conducted at a higher temperature than
that of the steam-bath some profound change occurs, but the matter
has not been further investigated.

Oxidation of Harmaline Methosulphate.—This methosulphate is
somewhat sparingly soluble in acetone, even on boiling, and sepa-
rates in short, well-developed, glistening prisms with bevelled
edges. For the purpose of oxidation, the methosulphate (1·5 grams)
was dissolved in the least possible quantity of boiling water, mixed
with acetone (40 c.c.), and cooled to −10°, during which some of the
methosulphate separated in a very finely divided condition. Pow-
dered permanganate (2·3 grams) was then gradually added, and so
soon as oxidation was complete the whole was filtered and the pre-
cipitate, which yields only a trace of acid on extraction with water
and acidifying, washed thoroughly with warm acetone. On concen-

trating the acetone extract on the steam-bath, a crystalline mass (0·4 gram) separated which, after recrystallisation from acetone, melted at 227° and consisted of ketoisonormethyltetrahydroharmine. (Found, $C = 67·9$; $H = 6·1$. $C_{13}H_{14}O_2N_2$ requires $C = 67·8$; $H = 6·1$ per cent.)

Reduction of Harmaline to Tetrahydroharmine.

Tetrahydroharmine, $C_{13}H_{16}ON_2$ (m. p. 199°), was first prepared by O. Fischer (*Ber.*, 1889, **22**, 637) by the reduction either of harmine or harmaline in alcoholic solution by sodium and later (*Ber.*, 1897, **30**, 2484) in *iso*amyl alcohol solution by sodium. We find that it may be readily prepared by the following simple process: Harmaline (5 grams), dissolved in water (100 c.c.) and hydrochloric acid (20 c.c.), is heated to boiling and then sodium amalgam (300 grams of 3 per cent.) added in three portions, together with further small quantities of hydrochloric acid, so that the liquid is always strongly acid. The deep yellow colour of the harmaline hydrochloride gradually disappears and the solution at the end is almost colourless. On cooling, the sparingly soluble hydrochloride of tetrahydroharmine separates in colourless crusts, and this is collected, dissolved in hot water, precipitated by ammonia, and the base crystallised from methyl alcohol, from which it separates in bundles of needles melting at 198—199°. (Found, $C = 72·3$; $H = 7·6$. $C_{13}H_{16}ON_2$ requires $C = 72·2$; $H = 7·4$ per cent.) A further quantity may be obtained from the original mother liquors of the hydrochloride, and the total yield is about 90 per cent. of that theoretically possible.

Oxidation of Tetrahydroharmine to Harmaline.— In this experiment tetrahydroharmine (2 grams), dissolved in acetone (150 c.c.), was cooled to −10° and then oxidised by the gradual addition of very finely powdered permanganate (4 grams). The oxidation takes place very gradually, and as soon as the permanganate has been completely decolorised, the whole is filtered and the acetone filtrate concentrated to a small bulk, when a mass of crystals separates which melt at 245° and consist of harmaline, as a mixed melting point and careful comparison of properties clearly demonstrated. (Found, $C = 73·2$; $H = 6·6$. $C_{13}H_{14}ON_2$ requires $C = 72·9$; $H = 6·6$ per cent.)

Conversion of Tetrahydroharmine into Methyltetrahydroharmine (m. p. 176°).

The methylation of tetrahydroharmine takes place readily under the following conditions: Tetrahydroharmine (3 grams), suspended

in benzene (10 c.c.), is stirred with methyl sulphate (3 c.c.), causing a considerable rise of temperature and separation of a syrup which consists mainly of the methyl hydrogen sulphate of methyltetrahydroharmine.

After twenty-four hours the benzene is decanted, the syrup rubbed and washed with ether, during which it becomes very viscid and stringy, but does not crystallise. This syrup, which contains some tetrahydroharmine methyl hydrogen sulphate or sulphate, was dissolved in water, in which it is very soluble, and mixed with ammonia, when a syrup separated which gradually crystallised. This was collected, dissolved in boiling methyl alcohol, cooled, and vigorously stirred, causing an appreciable amount (about 0·3 gram) of tetrahydroharmine to separate, which was removed by filtration.

The filtrate was allowed to evaporate and the residual pale brown syrup rubbed with a few drops of methyl alcohol, when it soon began to crystallise and, after remaining in contact with porous porcelain and recrystallisation .first from benzene and then from methyl alcohol, a colourless mass of needles was obtained which melted at 174—176°, and consisted of methyltetrahydroharmine (Found: $C = 73\cdot3$; $H = 7\cdot9$. $C_{14}H_{18}ON_2$ requires $C = 73\cdot1$; $H = 7\cdot8$ per cent.).

The Behaviour of Harmine Derivatives with Diazonium Salts.

Harmine, harmine methosulphate, methylharmine, methylharmine methosulphate, methylharminesulphonic acid, norharmine, and methylnorharmine do not react with benzenediazonium chloride, p-nitrobenzenediazonium chloride, or diazobenzenesulphonic acid in aqueous acid, alkaline, or neutral solution. O. Fischer and Boesler (loc. cit.) have shown that harmaline forms bisazo-derivatives, and for the sake of comparison with p-nitrobenzeneazotetrahydroharmine we prepared the condensation products from harmaline and harmaline methochloride with p-nitrobenzenediazonium chloride in dilute acetic acid solution in the presence of sodium acetate. Harmaline gave a dark chocolatebrown precipitate, which appeared slowly and dissolved in concentrated sulphuric acid to a fine, intense royal-blue solution, which, on keeping, became successively dull reddish-purple, reddish-brown, and brown. Harmaline methochloride under similar conditions gave an almost black precipitate, which dissolved in sulphuric acid to a blue solution which, on keeping, became bluish-green, olivegreen, and finally dull brown. Methylharmalinesulphonic acid (or harmaline-methohydroxide-sulphonic anhydride) also condenses

with diazonium salts in alkaline solution, and with tetrazotised benzidine yields a dull reddish-purple solution with very deep green fluorescence. On the addition of acid, the solution becomes orange-yellow and the fluorescence disappears, but the alkaline solution dyes cotton in dull mauve shades unaffected by acid. Tetrahydroharmine and *N*-methyltetrahydroharmine condense immediately with diazonium salts in acetic acid solution. With tetrazotised benzidine either of these bases gives a bright red precipitate which dissolves in dilute hydrochloric acid to a reddish-purple, bluish-purple, or pure blue solution according to the concentration of the acid. In concentrated sulphuric acid the solution is pure blue. A dilute acid solution dyes cotton in intermediate shades. The dyed fabric becomes blue if placed in moderately concentrated hydrochloric acid, and on washing with water the colour changes to terra-cotta. Cotton is also dyed terra-cotta by an alcoholic solution of the azo-derivative. With simple benzenediazonium salts, tetrahydroharmine gives yellow to orange precipitates, whilst with those derived from naphthylamines the colour is usually red.

p-Nitrobenzeneazotetrahydroharmine,

is obtained as a reddish-brown precipitate on the addition of a solution of *p*-nitrobenzenediazonium acetate to an aqueous acetic acid solution of tetrahydroharmine. Tetrahydroharmine (0·216 gram) was dissolved in water (10 c.c.) and acetic acid (2 c.c.). *p*-Nitroaniline (0·272 gram : 2 mols.) was dissolved in warm concentrated hydrochloric acid (3 c.c.), diluted with water (10 c.c.), and diazotised by the addition of sodium nitrite, after which the solution was made up to 25 c.c. by the addition of saturated aqueous sodium acetate solution. One half exactly of the diazotised *p*-nitroaniline solution was then added to the tetrahydroharmine solution, and after one minute the precipitate was collected, thoroughly washed with water, dried at 100° and in a vacuum over phosphoric oxide until constant. The amount obtained was 0·340 gram, which is a yield of 93 per cent. of the theoretical. The filtrate contained no diazonium salt and, on the addition of the second half of the diazotised *p*-nitroaniline, there was a small precipitation of azo-derivative, but on adding an amount of tetrahydroharmine, dissolved in dilute acetic acid, judged to be approximately 0·2 gram, there was a voluminous precipitate. This experiment proves that the condensation occurs between one molecule of the base and one

of the diazonium salt. The substance is soluble in boiling alcohol
to a crimson solution and, on allowing to cool slowly, the greater
part separated in an unsatisfactory condition, but the black
powder was mixed with some long, coal-black needles which formed
aggregates that could be separated mechanically. These were dried
in a vacuum over sulphuric acid and analysed :

0·1147 gave 0·2638 CO_2 and 0·0554 H_2O. $C = 62·7$; $H = 5·4$.

$C_{19}H_{19}O_3N_5$ requires $C = 62·5$; $H = 5·2$ per cent.

p-*Nitrobenzeneazotetrahydroharmine* melts at 173—175° with
decomposition to a black froth. It dissolves in concentrated hydro-
chloric acid to a crimson solution which becomes orange-red when
greatly diluted with water. Unlike the nitrobenzeneazo-derivatives
from harmaline and methylharmaline, the solution in sulphuric
acid is carmine and does not change appreciably on allowing to
remain. The black needles give a chocolate smear on paper, and
this exhibits a beetle-green lustre. Methyltetrahydroharmine yields
a very similar substance on coupling with diazotised p-nitroaniline,
whilst methyltetrahydroharmine methosulphate in dilute acetic acid
solution in the presence of sodium acetate yields an orange-red
solution on the addition of p-nitrobenzenediazonium acetate, and
this solution becomes blood-red on making alkaline with sodium
hydroxide. The base, melting at 129°, obtained from the latter
methosulphate by the action of alcoholic potassium hydroxide
(p. 956), yields in acetic acid solution an orange-red liquid which
becomes carmine on the addition of hydrochloric acid.

Benzeneazotetrahydroharminesulphonic Acid,
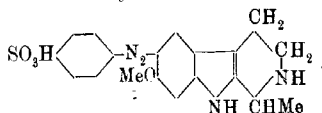
Tetrahydroharmine (1 gram) in dilute acetic acid (100 c.c.) was
mixed with a solution of diazobenzenesulphonic acid (from 1 gram
of sulphanilic acid) when an orange liquid was obtained, and in a
few minutes an orange-yellow azo-compound separated in glistening,
microscopic prisms. The substance was collected and purified by
solution in dilute aqueous sodium hydroxide and precipitation by
the addition of acetic acid. The crystals were collected, washed
with water, and dried at 100° :

0·2860 gave 0·1658 $BaSO_4$. $S = 8·0$.

$C_{19}H_{20}O_4N_4S$ requires $S = 8·0$ per cent.

The substance is not soluble in cold sodium carbonate solution and is very sparingly soluble in organic solvents even in boiling glacial acetic acid. It dissolves in aqueous sodium hydroxide to a bright orange-yellow solution, and this becomes crimson on the addition of hydrochloric acid. The change is very similar to that which is exhibited by methyl-orange when treated in a similar manner, but the harmine derivative gives a more intense colora-tion. It is, however, not so sensitive an indicator as methyl-orange and requires a higher concentration of hydrogen ion in order to effect the change of colour. A crimson acid solution was diluted with water until the colour had become orange-brown, and on the addition of a trace of methyl-orange the crimson colour was restored. Silk and wool are dyed in pale yellow shades from a sus-pension of this substance in hot dilute acetic acid.

Benzeneazomethyltetrahydroharminesulphonic Acid.

This substance was prepared from methyltetrahydroharmine in exactly the same way as described above for the corresponding tetra-hydroharmine derivatives. The only difference noted was that it crystallised more slowly from solution and had a reddish-brown colour. In acid and alkali it behaved exactly as the substance just described:

0.3142 gave 0.1787 $BaSO_4$. $S = 7.7$.

$C_{20}H_{22}O_4N_4S$ requires $S = 7.8$ per cent.

It is an interesting circumstance that the basic nitrogen atom of tetrahydroharmine is not concerned in the coupling with diazon-ium salts, and this follows from the observation that N-acetyl tetra-hydroharmine, which does not dissolve in dilute acids, condenses with diazobenzenesulphonic acid in aqueous acetic acid solution with the formation of an azo-derivative which is crimson in acid and yellow in alkaline solutions. The oxidation product of har-maline methosulphate, keto*iso*normethyltetrahydroharmine (m. p. $228°$, p. 960), does not condense with diazonium salts.

Colour Reactions for Indole Derivatives applied to Degradation Products of Harmine.

O. Fischer (*Ber.*, 1897, **30**, 2484) noted that tetrahydroharmine colours a pine shaving green in hydrochloric acid solution and that dihydroapoharmine (*Ber.*, 1889, **22**, 640) under the same condi-tions produces an orange colour, but these reactions are not very

N N

characteristic, and we have tried to obtain more definite evidence that harmine is an indole derivative. Almost all the hydro-derivatives give indole indications after fusion with potassium hydroxide, but we specifically mention only those examples which are characteristic. Keto*iso*normethyltetrahydroharmine (m. p. 228°, p. 960), obtained by the oxidation of harmaline methosulphate, is very stable towards fusion with potassium hydroxide, and remains for some time as a yellow or yellowish-brown oil. At a certain point the mixture froths and becomes almost homogeneous and the reaction is then finished. Water is added and the liquid extracted with ether. The colourless, ethereal solution is washed with dilute hydrochloric acid and evaporated, when a small residue is obtained, and this colours a wood ·shaving blue, in alcoholic hydrochloric acid solution, and gives a deep blue coloration with *p*-dimethylaminobenzaldehyde and aqueous-alcoholic hydrochloric acid on gently warming. The ethereal solution evidently contained a neutral indole derivative, and this was confirmed by treating another portion with concentrated hydrochloric acid and vanillin, when a crimson solution was obtained. Still another portion was dissolved in sulphuric acid to an orange-red solution, which on the addition of a trace of glyoxylic acid (obtained by adding magnesium powder to a concentrated aqueous solution of oxalic acid) became brownish-purple. The hydrochloric acid washings of the ethereal extract were rendered alkaline with sodium hydroxide and extracted with ether. After removal of the solvent the colour reactions just described could be obtained. The fusion of the substance melting at 228°, with potassium hydroxide, results, therefore, in the production of a basic and a neutral indole derivative. The colour obtained with *p*-dimethylaminobenzaldehyde indicates that an α-position has been set free in the indole ring, since scatole gives a blue coloration with this reagent, whilst α-methylindole gives a crimson colour and its methylenedioxy-derivative (Foulds and Robinson, T., 1914, **105**, 1969) almost an identical shade, showing that alkyloxy-groups in the ring are not likely to modify these colour reactions to any great extent. When *iso*methyltetrahydroharmine methohydroxide methyl ether (m. p. 129°, p. 956), obtained from methyltetrahydroharmine methosulphate by the action of methyl-alcoholic potassium hydroxide, is fused with alkali in the presence of air at a high temperature and the product subsequently treated with water, acidified, and the solution evaporated to dryness, a mauve-red coloration is obtained in the test with *p*-dimethylaminobenzaldehyde. This indicates the production of an indole derivative with a free β-position. The base, melting at

129°, and also *N*-acetyltetrahydroharmine yield, beyond question, indole derivatives when warmed with concentrated hydrochloric acid. The acetyl derivative gives a deep greenish-blue coloration when heated with hydrochloric acid and then mixed with an alcoholic solution of *p*-dimethylaminobenzaldehyde.

Either compound when heated with concentrated hydrochloric acid for thirty seconds and then treated with a little vanillin gives a most intense permanganate-coloured solution and, on the addition of water, a purple precipitate. Tetrahydroharmine itself gives a somewhat similar, but far weaker, reaction and a colourless substance separates. On adding water the latter remains unchanged, but most of the colour of the liquid is discharged. With vanillin and hydrochloric acid, α-methylindole gives an orange colour and β-methylindole a blue solution.

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[*Received, June 23rd,* 1919.]

LXXX.—*Harmine and Harmaline. Part IV.*

By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

IN Part III. of this research (this vol., p. 937) it was argued that harmine must be represented by one of the formulæ I or II, and evidence was brought forward which was interpreted in favour of the first of these alternatives:
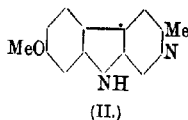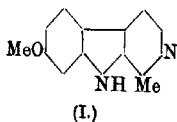
The corresponding expressions for the base, harman, which O. Fischer (*Chem. Centr.*, 1901, i, 957) obtained by eliminating the methoxyl group from harmine are III and IV respectively. In the communication already quoted (p. 945) the present authors also considered the question of the probable nature of a base, $C_{12}H_{10}N_2$, prepared by Hopkins and Cole (*J. Physiol.*, 1903, **29**, 451) from

tryptophan by oxidation with ferric chloride, and suggested the representations III and V, of which the former was preferred:
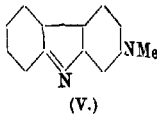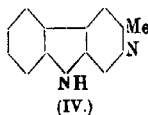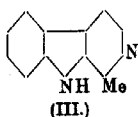
The possibility was therefore mooted that the base, $C_{12}H_{10}N_2$ (m. p. 238°), might prove to be harman (m. p. 230° according to O. Fischer, *loc. cit.*), and we are now able to state that this is actually the case. We are greatly indebted to Professor F. Gowland Hopkins, F.R.S., for a specimen of the base, $C_{12}H_{10}N_2$, and, as the result of a careful comparison, we can detect no difference between this substance and harman, the melting point of which we find is also 238°. The details are given in the brief experimental portion appended, and some of the theoretical consequences of this interesting result may now be considered. In the first place this conjunction of the chemistry of harmine and of tryptophan very much strengthens the case for acceptance of the formula I as the best summary of the relations of harmine, since it is almost inconceivable that a substance constituted as IV could arise from tryptophan, even in the presence of other substances. The only loophole is the possible occurrence in some specimens of this amino-acid of a methyltryptophan (VI), which is extremely improbable:
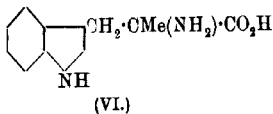
Secondly, the theory put forward in our preceding memoir (*loc. cit.*, p. 944) that harmine originates in nature from a hydroxytryptophan receives important confirmation, since harman may now be so simply obtained from tryptophan in the laboratory. Clearly the mechanism of the latter reaction is a matter worthy of close investigation, since it is probably on analogous lines to the vital synthesis of an alkaloid. One possibility is expressed in the following scheme, in which tryptophan alone is supposed to yield the base and in which the unusual fission, occurring at the point indicated by the dotted line, may find some analogy in the decomposition of tryptophan by *B. coli* resulting in the formation of indole without scatole:
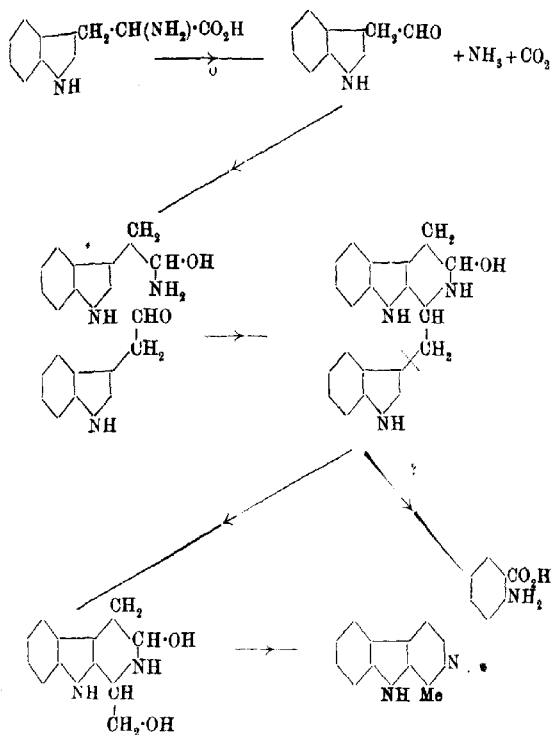
On the other hand, it is more probable that the Me·C group is introduced as the result of the participation in the reaction of some substance which can yield acetaldehyde on oxidation, and as alanine is such a compound it appears feasible to suggest that harman is the result of the oxidation of a mixture of tryptophan and alanine or equivalent dipeptides containing tryptophan and alanine units. The process could then be represented in the manner shown on p. 970.

There are naturally other possibilities, such as the presence of ethyl alcohol or acetic acid.

The fused benzene–pyrrole–pyridine nucleus which it now seems certain is contained in the molecule of harmine does not find a place in any approved system of nomenclature, and we therefore suggest

$$\text{CH}_2\cdot\text{CH(NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$$

$$\text{NH}$$

$$\text{NH}_3 + 2\text{CO}_2 + \quad \begin{array}{c} \text{CH}_2 \\ \text{CH}\cdot\text{OH} \\ \text{NH}_2 \\ \text{CHO} \\ \text{Me} \end{array} \quad \xrightarrow{-2\text{H}_2\text{O}} \quad \text{NH CHMe}$$

$$\text{NH Me}$$
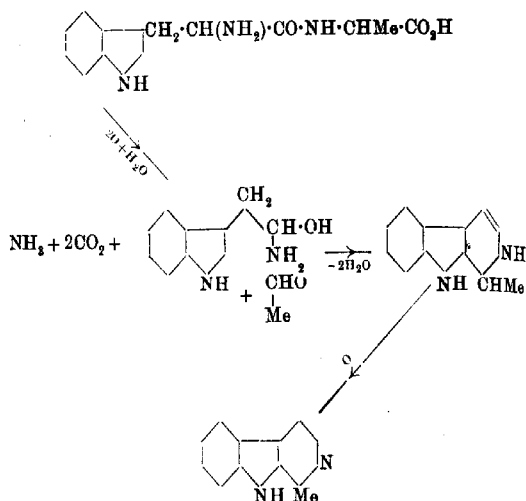
the name '*carboline*'* for this structure, indicating an analogy both to carbazole and quinoline. There are four carboline substitution products and these may be named in accordance with a scheme of numbering which is the same in all cases, and is indicated below in the case of 4-carboline (*nor*harman):
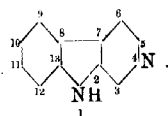
4-Carboline.
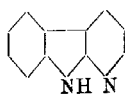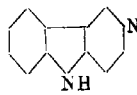
3-Carboline.   5-Carboline.   6-Carboline.
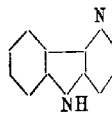
Isomeric and probably tautomeric with these are the four 'isocarbolines,' the numbering of which need not differ from that of the carbolines. Thus harmine is 11-methoxy-3-methyl-4-carboline,

* The term " carbazoline " has already been used to denote reduction products of carbazole (compare Carrasco, *Gazzetta*, 1908, **38**, ii, 301).

whilst methylharmine (VII, compare this vol., p. 942) is
11-methoxy-3:4-dimethyl-4-*iso*carboline:

Meo⟨ ⟩NMe   N⟨ ⟩
    N   Me   Me   NH
   (VII.)   (VIII.)
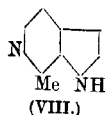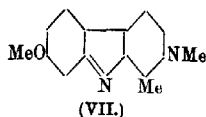
*apo*Harmine, it may be pointed out, has now been shown to be
8-methyl-7-pyrindole (VIII) in accordance with the nomenclature
previously suggested (T., 1912, **101**, 1787) for fused pyrrole–pyr-
idine nuclei.

EXPERIMENTAL.

O. Fischer (*loc. cit.*) converted harmine into the corresponding
phenol, harmol, by demethylation with concentrated hydrochloric
acid in a sealed tube at 140—170°. We have employed this method
also, but, in addition, have prepared harmol in almost theoretical
yield by boiling harmine with an excess of hydriodic acid (D 1·7)
during five hours. On dilution with water and the addition of
enough sulphurous acid to remove the free iodine, a crystalline pre-
cipitate remained and this was collected and dissolved in dilute
aqueous sodium hydroxide. The filtered solution was acidified with
acetic acid and the harmol precipitated by the addition of ammonia.
The base was at first somewhat viscid, but very soon became granu-
lar and crystalline, and was then collected, washed with water, and
dried at 100°. Harmol may be converted into harman by careful
distillation with a very large excess of zinc dust in a stream of
hydrogen, but owing to the high melting point of harmol the yield
is unsatisfactory. The crude product from the distillation of
15 grams of harmol, intimately mixed with 250 grams of zinc dust,
was dissolved in the minimum of cold concentrated sulphuric acid
and the diluted solution mixed with insufficient aqueous ammonia
to neutralise the acid. The sparingly soluble sulphate, which
separated almost immediately, was collected and decomposed by
aqueous sodium hydroxide, when the recovered base, after three
crystallisations from benzene, melted at 238°. Harman was also
prepared by O. Fischer's method from aminoharman and, as it was
thought that the product might be contaminated with ethylharmol,
it was boiled with an excess of concentrated hydriodic acid during
an hour and the solution diluted, treated with sulphurous acid, and
finally with an excess of sodium hydroxide. The precipitated base
was collected, crystallised from benzene, and obtained in prisms
melting at 238° alone or mixed with a specimen of harman pre-

pared as described above. The specimen of the base $C_{12}H_{10}N_2$ which Professor Hopkins kindly sent us melted at 238° after two crystallisations and the melting point was not depressed by intimate mixture with an approximately equal amount of pure harman. Harman crystallises from benzene in well-defined prisms, the *sulphate*, from dilute sulphuric acid, in radiating clusters of short, delicate, microscopic needles and the *mercurichloride* from dilute hydrochloric acid containing mercuric chloride in long, slender needles. Under the microscope the latter are seen to extend across the field, and each crystal presents the appearance of two sharply defined, straight, parallel lines very close together. The respective crystalline forms and approximate solubilities of the base from tryptophan and its sulphate and mercurichloride were carefully compared with those of harman and the two salts thereof, with the result that complete identity was observed. O. Fischer states that solutions of salts of harman fluoresce blue, but we consider that it is violet, and the shade and intensity of fluorescence were identical in the cases of solutions of harman and of the base from tryptophan. The following experiments were carried out with both specimens and identical results observed. A trace of harman was boiled during five minutes with an excess of methyl iodide, after which the mixture was evaporated to dryness. The pale yellow residue which was sparingly soluble, even in boiling water, was heated with an aqueous suspension of freshly precipitated silver chloride and the solution filtered. The colourless aqueous solution of harman methochloride so obtained exhibited a bluish-violet fluorescence. On the addition of a drop of aqueous sodium hydroxide there was no precipitate, but, on the further addition of sodium hydroxide, a pale yellow precipitate was obtained. On shaking with benzene the latter extracted a bright yellow substance and the solution had a green fluorescence.

The benzene extract was separated and, on the addition of dilute hydrochloric acid, became colourless and the aqueous layer acquired a violet fluorescence. When harman is heated with phthalic anhydride a yellowish-brown fusion is obtained, and, on boiling with alcohol and cooling the solution, a sparingly soluble, orange, crystalline substance separates. The reaction is probably due to a condensation which involves the methyl group in the α-position in the pyridine ring, and harmine exhibits a quite similar behaviour.

Organic Chemistry.

The Atom Model of Rutherford and Bohr in Chemistry.
A. E. LACOMBLÉ (*Chem. Weekblad*, 1919, **16**, 832—834).—A dis-
cussion of various difficulties which arise in the further development
of the ideas suggested by Buchner (this vol., i, 245) in his applica-
tion of the Rutherford-Bohr theories of atomic structure to the case
of atom linking in organic compounds. If the single bond between
two carbon atoms be constituted by the attraction of two valency
electrons revolving in an orbit perpendicular to the line joining the
two positive nuclei, then, in addition to the electrostatic field, an
electromagnetic field is established the direction of which is deter-
mined by the sense of the motion of the electrons in the orbit. In
the case of the methane molecule there would thus be several
possible isomerides owing to the possibility of positive or negative
rotation of the electrons in the four atomic bonds as viewed from
the carbon nucleus. Two of these isomerides are symmetrical, the
rotations in one being all positive and in the other all negative.
These are enantiomorphous isomerides, and each gives rise to one
derivative of the formula CH_3R and one CH_2R_2. The unsymmetri-
cal possibilities may be represented as $+ + + -$, $+ + - -$,
$+ - - -$. Each of these gives two isomeric mono-derivatives of the
formula CF_3R. As these are unknown, it may be assumed that
only the symmetrical forms exist. In chains of carbon atoms
"positive" carbon atoms must alternate with "negative" atoms, so
that a closed ring is only possible with an even number of atoms,
unless for the odd atom an abnormal structure is assumed, which
would again render possible the existence of unknown isomerides.
It is also pointed out that the displacement of the electrons to form
orbits between the carbon atoms of the diamond would probably
be indicated in the Röntgen diagram of the crystal by the presence
of lines. Such lines have not been observed. W. S. M.

The Nature of the Ethylenic and Acetylenic Linkings in
Carbon Compounds. W. E. GARNER (*Chem. News*, 1919, **119**,
16—17).—The appearance or disappearance of the unsaturated
linking in carbon compounds is generally accompanied by *trans*-
elimination or *trans*-addition of the groups leaving or entering the
molecule. An explanation of the mechanism of such reactions is
offered in terms of Bohr's theory of the arrangement of the atoms
and electrons in the molecule. It is shown by means of diagrams
that when two univalent atoms, for example, hydrogen and
bromine, become detached from two adjacent carbon atoms, with
formation of an ethylenic linking, this is more likely to occur in the
trans- than in the *cis*-position. E. H. R.

New Practical Method of Carbonising Coal at Low
Temperatures. FRANZ FISCHER and W. GLUUD (*Ber.*, 1919,
52, [B], 1035—1039).—Difficulties are encountered in carbonising

considerable quantities of coal at low temperatures in a reasonable time since, owing to the low thermal conductivity of the material, the heat penetrates so slowly into the interior of the charge that the outer portions readily become overheated. The authors consider that the conditions essential for success are that the volatile portions should not be heated to a temperature higher than that necessary for their volatilisation and that they should not be exposed to this temperature for an unnecessarily long period. They have therefore constructed a cylindrical retort which can be rotated round a horizontal axis. The latter is hollow, but is plugged in the middle. Through the one end steam is admitted which carries off the volatile products through the other end to a suitable condensing arrangement. The furnace is heated from underneath by a series of gas burners fed with air under pressure, whilst loss of heat is prevented by enclosing the furnace with a metal sheath. A thermo-couple is placed in the axis. The furnace permits the distillation of 20 kilos. of coal in one to two hours. Distillation generally commences at about 350° and is complete at 500°. The yield of tar is 3—30%, according to the kind of coal used. The first portions of the oils are lighter than water, the last portions are heavier, the mean density being slightly greater than unity. The tar appears in thin layers as a golden-red oil, which is more or less viscous according to the kind of coal used.   H. W.

Paraffin from Coal. W. GLUUD (*Ber.*, 1919, **52**, [*B*], 1039—1053).—The occurrence of paraffin in low-temperature tars has been frequently noted, but little is known as to the nature of the individual components. The author has therefore investigated the tar derived from a Mond gas plant fed with a gas coal and finds the paraffin to be a mixture of saturated normal paraffins terminating with $C_{29}H_{60}$, in which hexa- and hepta-cosane preponderate. The series thus appears to be less comprehensive than with brown coal paraffins.

[With FRL. HENNY HÖVERMANN.]—The paraffin exists as such in the crystalline state in the tar, from which it is isolated by treatment of the latter with acetone; in the earlier experiments attempts were made to isolate a pure product by repeated crystallisation of the crude substance, first from acetone and subsequently from benzene. In this manner, heptacosane was ultimately isolated. Better results, however, were obtained by repeated fractional distillation of the crude product under diminished pressure and crystallisation of the individual fractions when necessary. The complete series from $C_{24}H_{50}$ to $C_{29}H_{60}$ could thus be isolated, the identity of the products being established by direct comparison with the synthetic substances. Heptacosane was prepared by the action of phosphorus pentachloride on myristone and treatment of the chloride with hydriodic acid; contrary to the usual assumption, however, the intermediate product was found to be *vχχ-trichloro-n-heptacosane*, needles, m. p. about 30°, the formation of which is attributed to the ketone reacting in its enolic form and addition of

chlorine occurring at a higher temperature. Octacosane was prepared in satisfactory yield by the electrolysis of a mixture of myristic and palmitic acids. The following constants are recorded for the synthetic hydrocarbons: $C_{26}H_{54}$, n_D^{65} 1·43332, n_C^{65} 1·43096, n_F^{65} 1·43851, n_D^{80} 1·42774, n_C^{80} 1·42534, n_F^{80} 1·43293 ; $C_{27}H_{56}$, n_D^{65} 1·43453, n_C^{65} 1·43228, n_F^{65} 1·43992, n_D^{80} 1·42874, n_C^{80} 1·42636, n_F^{80} 1·43411 ; $C_{28}H_{58}$, n_D^{65} 1·43539, n_C^{65} 1·43309, n_F^{65} 1·44071, n_D^{80} 1·42971, n_C^{80} 1·42737, n_F^{80} 1·43501.

Investigation of the paraffins obtained from other varieties of coal rendered it very probable that they are closely similar in composition. The isolation of small amounts of paraffin by the direct extraction of coal with benzene at 260—270° leads the author to the conclusion that it exists in all probability to some extent as such in coal, and is therefore not exclusively a product of secondary processes occurring during distillation. H. W.

Light Petroleum from Coal. FRANZ FISCHER and W. GLUUD (*Ber.*, 1919, **52**, [*B*], 1053—1068).—The object of the investigation was to get a general insight into the nature of the most volatile fractions of low-temperature tar. It was found that considerable quantities (about 1% of the weight of the coal) of light petroleum could be obtained, and that benzene is not present in more than minimal amount.

Three different coals were investigated, a gas coal (Zecke Lohberg) and two fat coals (Flöz Albert and Minden). The latter was of interest, since the mine from which it was obtained was known to smell of petroleum; the coal evolved paraffins at a temperature well below that at which carbonisation commenced, so that it is established that light paraffins can exist pre-formed in certain coals. The light petroleum was isolated from the gas and also from the tar. In the former case, since it was desired to operate in a technical manner, extreme cooling as with liquid air was not adopted; the products were isolated either by liquefaction by compression in steel cylinders or, preferably, by compression into paraffin oil and isolation from the latter by treatment with steam. In this manner the considerable fraction boiling below 20° was lost; the product had b. p. 20—100° with only small portions of higher boiling point. The tar was treated with steam and the distillation was discontinued when only small quantities of oil came over, since otherwise considerable quantities of phenolic substances distilled. The boiling point of the distillate was mainly 60—200°. All the fractions contained sulphur compounds. They were purified by treatment with alkali and then with concentrated and 15% fuming sulphuric acid or, preferably, with aluminium chloride; the use of liquid sulphur dioxide proved less advantageous. Perfectly colourless liquids were thus obtained, which were stable towards light and air. The fraction, b. p. 20—60°, was composed of saturated paraffin hydrocarbons; that of b. p. 60—100° contained naphthenes mixed in the case of the gas coal with paraffins. The composition of the higher fractions, b. p.'s 100—125° and 125—190°, was less definite; they

appeared to be mixtures of paraffins with naphthenes with higher hydrogen content and, probably, complex aromatic compounds.

The fractions, b. p. 60—100°, were examined for benzene; the presence of the latter in small amount was established in a product obtained from the Minden coal and purified with liquid sulphur dioxide, the isolation being directly effected by exposure to low temperature, but the quantity present cannot exceed 3%. The fractions obtained from the second fat coal and from gas coal and purified by aluminium chloride appeared to be free from benzene when examined by the triphenylmethane method. The usual identification by successive conversion into nitrobenzene and aniline appeared inadmissible in this instance owing to the danger of the formation of benzene by the oxidation of more highly hydrogenated products.

The behaviour of the several fractions when cooled has also been fully investigated; the original paper must be consulted for details.

H. W.

Preparation of some Volatile, Saturated Acyclic or Cyclic Hydrocarbons contained in Light Petroleums. G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, **168**, 1324—1326).—A number of aliphatic and cyclic hydrocarbons have been prepared and their b. p.'s, densities, and critical temperature of solution in aniline determined. The following results were obtained:

	Crit. temp. sol. in aniline.	B. p.	Density.
Pentane	72·0°	36·3°	D_0^4 0·6454
isoPentane	77·0	28·0	D_0^4 0·6394
isoHexane	73·8	61·7—62·4	D_{15}^4 0·658
isoHeptane	72·8	90—91	D_{15}^4 0·6842
Heptane	70·0	98—98·3	D_{15}^4 0·0879
Octane	71·8	125·8	D_{15}^4 0·7063
Methylcyclohexane	41·0	100·4	D_0^4 0·780
1 : 2-Dimethylcyclohexane	42·1	128·6—129	D_{15}^4 0·798
1 : 3-Dimethylcyclohexane	49·7	121·2—121·8	D_{15}^4 0·775
1 : 4-Dimethylcyclohexane	48·0	122·7—123	D_{15}^4 0·783
cycloPentane	18·0	49·5	D_{15}^4 0·750
Methylcyclopentane	35·0	72·0	D_{15}^4 0·753

The authors find that, for the conversion of butyric, adipic, or methyladipic acid into its corresponding ketone, manganous carbonate is a very effective catalyst.

W. G.

Decomposition of Acetylene at High Temperatures in the Presence of Various Catalysts. SIEGFRIED HILPERT (*Ges. Abhand. Kennt. Kohle*, 1917, **1**, 271—275; from *Chem. Zentr.*, 1919, i, 709—710).—Experiments were undertaken with the object of polymerising acetylene to benzene, but a relatively satisfactory yield of the latter could not be obtained. In all cases, primary decomposition appears to involve the separation of carbon, and the formation of tar or benzene appears to be a secondary change. The acetylene was prepared from calcium carbide and purified by

passage over a long layer of kieselguhr impregnated with a solution of cuprous chloride in hydrochloric acid. The furnace consisted of an electrically heated Jena-glass tube. With coke as catalyst, it was found that the impurities in the material, particularly sulphur, took part in the change. With glass splinters, a fog of tar appeared at 400°, whilst at 500° a layer of carbon was slowly formed on the glass and a mixture of benzene and tar containing unsaturated substances was obtained; the decomposition of acetylene on glass appeared to be characterised by the formation of carbon at a relatively high temperature and the simultaneous production of tar. With powdered iron and more markedly with nickel, decomposition commenced at 300° and proceeded so rapidly at 400° that the tube rapidly became choked with carbon; the tar was strongly unsaturated and contained but little benzene. Aluminium, mercury, lead, zinc, and tungsten had little action. With copper a brown deposit rapidly formed, which soon choked the tube completely, whilst an unpleasant smelling tar was formed in small amount. Brass filings, on the other hand, only became slowly coated with carbon and gave a tar similar to that obtained with glass. Molten phenanthrene or anthracene did not react with acetylene in the presence or absence of aluminium chloride.　　　　　　　　　　　　　　　　　　H. W.

The **Interaction of Acetylene and Mercuric Chloride.** DAVID LEONARD CHAPMAN and WILLIAM JOB JENKINS (T., 1919, **115**, 847—849).

Action of Methyl Sulphate on the Alkali and Alkali-earth Sulphates. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, **168**, 1204—1206. Compare this vol., i, 308).—The alkali and alkali earth sulphates if heated with methyl sulphate in sealed tubes at varying temperatures yield the pyrosulphate of the metal and dimethyl ether. This is shown to be due to the direct interaction of the two sulphates, and not to the intermediate formation of a sulphate such as sodium methyl sulphate, which would subsequently break down to the pyrosulphate and methyl ether. W. G.

The Hydrolysis of Ethyl Sulphite. A. BAGGESGAARD-RASMUSSEN (*Ber.*, 1919, **52**, [*B*], 1069—1078).—The work of previous investigators has shown definitely that ethanesulphonate is formed in small amount during the hydrolysis of ethyl sulphite by alkali hydroxide, but an explanation of the phenomenon has not been given. The author has performed a series of quantitative experiments under different conditions, and has measured both the amount of base unused and the quantity of sulphite formed; the extent of hydrolysis as indicated by the first method is invariably slightly greater than that shown by the second, but a part of the difference is to be ascribed to an unavoidable slight oxidation of the sulphite. The actual formation of sodium ethanesulphonate is, however, placed beyond doubt. The author finds that the hydrolysis of ethyl sulphite by bases is in the main an absolutely

normal process; if, however, the action occurs slowly (as with the equivalent amount of alkali), small quantities (about 4—5%) of ethanesulphonate are produced. This compound is shown to be formed by the action of ethyl sulphite on the alkali sulphite first produced.   H. W.

Biochemical Formation of Mercaptans. F. F. Nord (*Ber.*, 1919, **52**, [*B*], 1207—1211).—Neuberg and Nord (A., 1914, i, 1046) have shown that thioacetaldehyde is reduced to ethyl mercaptan by living yeast and also by zymase solution. The present investigation deals with the possibility of a similar process occurring with higher thioaldehydes. For biochemical purposes, it is unnecessary to isolate the difficultly accessible thioaldehydes in a state of purity; it is sufficient to treat the aldehydes with an alcoholic solution of ammonia and hydrogen sulphide, when homologues of thialdine are produced which behave as if they were mixtures of thioaldehyde and aldehydeimine, and possess the further advantage of being freely soluble in aqueous alcohol. *n*-Butaldehyde was treated in this manner and the product added to a solution of sugar in water which was undergoing brisk fermentation by yeast. Hydrogen sulphide was freely evolved, and, after fermentation had ceased, the liquor was found to contain *n*-butyl mercaptan, b. p. 95—102°, in small amount, together with indefinite compounds of higher boiling point. The presence of acetaldehyde was also established. In a similar manner, *isoamyl* mercaptan, b. p. 115—119°, was obtained from *iso*valeraldehyde: the thiovaleridine had a marked inhibitive action on the fermentation.   H. W.

Interaction of Mercuric and Cupric Chlorides Respectively and the Mercaptans and Potential Mercaptans. PRAFULLA CHANDRA RÂY (T., 1919, **115**, 871—878).

Water of Crystallisation : Compounds with 2H₂O and 3H₂O. I. GUARESCHI (*Gazzetta*, 1919, **49**, i, 134—140. Compare A., 1915, ii, 774).—Strontium formate loses its 2H₂O either (1) at 30°, or (2) at the ordinary temperature and a pressure of 20 mm. and in presence of sulphuric acid, the last ½H₂O being given up only very slowly; the anhydrous salt does not recover the water of crystallisation in the air. Zinc formate (+2H₂O) loses its water at 70° (not at 60°), the anhydrous salt reabsorbing about 1½H₂O from the air. Manganese formate loses its 2H₂O only at 70°, the last ½H₂O very gradually. Calcium chlorate (+2H₂O) undergoes complete dehydration at 50°, the anhydrous salt recovering all its water and then deliquescing in the air. Potassium ferrocyanide (+3H₂O) loses its water of crystallisation entirely either (1) at 50°, or (2) at 42° in a current of air, or (3) at the ordinary temperature in a desiccator over calcium chloride; in all cases the last ½H₂O is released extremely slowly.

From the observation that many salts appear to yield their water

of crystallisation in definite fractions, the conclusion is drawn that the true molecular weights for the hydrated salts are multiples of those corresponding with the simplest empirical formulæ.

T. H. P.

The Solubility of Silver Acetate in Acetic Acid and of Silver Propionate in Propionic Acid. JOSEPH KNOX and HELEN REID WILL (T., 1919, **115**, 853—854).

Stearic and Palmitic Esters of the Isomeric Propylene Glycols. L. ISABEL HOWE (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 13—18. Compare Ruttan and Roebuck, A., 1916, i, 115).—The 1:2- and 1:3-dihydroxypropanes may be directly esterified at high temperatures if constantly stirred, the optimum temperature of esterification varying with the acid used. After fusion, the mixture is freed from glycol by washing with hot water and from free acid by means of sodium hydrogen carbonate. The mono- and di-acid esters are separated by means of their different solubilities in alcohol. The following esters are described:

Propylene monostearate, $OH\cdot CHMe\cdot CH_2\cdot C_{18}H_{35}O_2$, had m. p. 59·5°, n^{60} 1·4424. The *distearate*, m. p. 72·3°, crystallised in large, flaky crystals, n^{75} 1·4366.

Trimethylene monostearate, $OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot C_{18}H_{35}O_2$, had m. p. 60·5°, n^{60} 1·4437, and the *distearate*, m. p. 64·7°, n^{75} 1·4397.

Propylene monopalmitate had m. p. 54·2°, n^{60} 1·4405, and the *dipalmitate*, m. p. 68·8°, n^{75} 1·4364.

Trimethylene dipalmitate had m. p. 56·2°, n^{75} 1·4374. The monopalmitate was not isolated.

W. G.

The Optically Active $\alpha\alpha'$-Dimethylglutaric Acids. ELOF MÖLLER (*Lunds. Univ. Årsskr.*, 1919, **15**, 56 pp.; from *Chem. Zentr.*, 1919, i, 606—608).—The author gives two tables of the known optically active dibasic acids with two similarly placed asymmetric carbon atoms, and points out the relationship between melting point and optical activity. There appears to be no connexion between the difference of melting point of the isomerides and the magnitude of the specific rotation. *r*-α*γ*-Dimethylglutaric acid has previously been resolved by means of the strychnine hydrogen salt, but the *l*-isomeride was not obtained pure (A., 1911, i, 12); the two antipodes have now been isolated in a state of purity, fission being effected with brucine or the α-phenylethylamines.

Ethyl r-αγ-dimethyl-α-carboxyglutarate,

$$CMe(CO_2Et)_2\cdot CH_2\cdot CHMe\cdot CO_2Et,$$
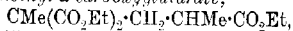
b. p. 156—158°/15 mm., is prepared by the action of ethyl β-bromo-*iso*butyrate on ethyl sodiomalonate; when hydrolysed with sodium hydroxide, it yields *r-αγ-dimethyl-α-carboxyglutaric acid* as a sticky mass of indefinite m. p. The saturated aqueous solution contains 159 grams per litre at 20°. The dissociation constant, $100k = 0.220$. The *potassium dihydrogen* salt forms long crystals,

the *dipotassium* salt cannot be prepared, whilst the *normal potassium* salt forms small, transparent crystals ($+H_2O$). Resolution of the acid could not be effected with α-phenylethylamine, quinine, or cinchonine, but was accomplished through the strychnine dihydrogen salts (the salt of the *d*-acid crystallises in colourless, anhydrous needles, that of the *l*-acid in prisms, $+4H_2O$). The active *acids* have m. p. 144—148°, $[α]_D^{20} +16\cdot3°$ and $-15\cdot6°$ in aqueous solution, and are more soluble in water than the racemic form.

r-αγ-Dimethylglutaric acid was partly resolved by strychnine and almost completely by brucine and the α-phenylethylamines, but not by cinchonine, cinchonidine, morphine, or quinine. With molar quantities of strychnine or brucine and *r*-acid, the salts of the *d*-acid separate first. *Strychnine* d-*αγ-dimethylglutarate* forms thin, transparent crystals ($+2H_2O$), solubility 2·4 grams in 100 grams water; the corresponding salt of the *l*-acid forms colourless threads, readily soluble in water. The brucine salt of the *d*-acid ($+2H_2O$) crystallises in colourless needles, 0·8 gram of which dissolves in 100 grams of water, whilst the salt of the *l*-acid forms transparent prisms, solubility 1·8 in 100. l-*Phenylethylamine* d-*αγ-dimethylglutarate* and d-*phenylethylamine* l-*αγ-dimethylglutarate* crystallise in needles, m. p. 157—158°, solubility 9 grams in 100 grams water; d-*phenylethylamine* d-*αγ-dimethylglutarate* and l-*phenylethylamine* l-*αγ-dimethylglutarate* have m. p. 144—145°, solubility 25 in 100. The strychnine salt of the *meso*-acid ($+2H_2O$) forms threads, solubility 12 in 100, whilst the brucine salt dissolves to the extent of 18 parts in 100. d- and l-*Phenylethylamine* meso-*αγ-dimethylglutarate* dissolve freely in water. *d*- and *l*-αγ-Dimethylglutaric acids crystallise in needles or prisms, $[α]_D^{20} +39\cdot8°$ in aqueous solution. Examination of the barium hydrogen salt shows that the univalent ion has the same sign of rotation as the parent acid, whilst the bivalent ion of the normal salt is optically inactive. The *l*-anhydride, obtained by the action of acetyl chloride on the *d*-acid at 50—60°, forms cubic crystals, m. p. 41·5—42·5°, $[α]_D^{19} -69\cdot6°$ in benzene solution, whilst the d-*anhydride* crystallises in slender needles, m. p. 42—43·5°, $[α]_D^{10} +69\cdot9°$ in benzene solution. The r-*anhydride*, prepared by admixture of its components (the *r*-acid is only attacked by acetyl chloride with difficulty), has m. p. 33—34°.

The product obtained by the elimination of carbon dioxide from optically active αγ-dimethyl-α-carboxyglutaric acid consists of a mixture of about 40% active and 60% *meso*dimethylglutaric acid: since the sign of rotation is the same as that of the carboxy-acid, it follows that the tri- and di-basic acids which rotate in the same direction are configuratively related.   H. W.

New ββ-Dialkylglutaric Acids. I. GUARESCHI (*Gazzetta*, 1919, **49**, i, 124—133. Compare A., 1901, i, 630).—The following further acids have been prepared by the method formerly used:

$\beta\beta$-Di-n-$propylglutaric$ $acid$, $CPr^2(CH_2\cdot CO_2H)_2$, prepared from $\alpha\gamma$-dicyano-$\beta\beta$-dipropylglutarimide, forms white crystals, m. p. 112—113°, and completely volatilises at a higher temperature, its vapour provoking coughing. The $ammonium$ salt is highly soluble in water, its aqueous solutions giving precipitates of various colours with salts of heavy metals.

β-$Ethyl$-β-$propylglutaric$ $acid$, $CEtPr(CH_2\cdot CO_2H)_2$, crystallises in colourless, flattened needles or long laminæ, m. p. 71—72°, and has an intensely acid reaction.

β-$Methyl$-β-$isobutylglutaric$ $acid$, $CHMe_2\cdot CH_2\cdot CMe(CH_2\cdot CO_2H)_2$, has m. p. 63—65°.

β-$Methyl$-β-$isohexylglutaric$ $acid$,

$$CHMe_2\cdot[CH_2]_3\cdot CMe(CH_2\cdot CO_2H)_2,$$

forms crystals, m. p. 62—63°; the $silver$ and $zinc$ salts were analysed.

β-$Methyl$-β-$nonylglutaric$ $acid$, $CH_3\cdot[CH_2]_8\cdot CMe(CH_2\cdot CO_2H)_2$, crystallises in broad, colourless laminæ, greasy to the feel, m. p. 46·5—47·5°.

β-$Methyl$-β-$hexylglutaric$ $acid$, $C_6H_{13}\cdot CMe(CH_2\cdot CO_2H)_2$, forms crystals, m. p. 52—53°.　　　.　　　T. H. P.

Manganous Tartrate and Potassium Manganous Tartrate.

LEONARD DOBBIN (*J. Amer. Chem. Soc.*, 1919, **41**, 934—940).— Manganous tartrate is prepared by adding an equimolecular solution of sodium or potassium tartrate to either manganous sulphate or chloride solutions, when, on keeping, small, rose-tinted crystals separate. The crystals are monoclinic with axial ratios $[a:b:c= 0·816:1:0·699, \beta=100°14']$. It loses 14% of its water at 100°, and continues to lose water up to 180°, and at 200° darkens with slight decomposition. The crystals have the formula $MnC_4H_4O_6,2H_2O$. All attempts by the author to prepare manganous potassium tartrate failed, hence it appears unlikely that this compound exists.

J. F. S.

New Explosive Substance Derived from Formaldehyde.

ANNIBALE MORESCHI (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 277—280).—The action of dry gaseous hydrogen chloride in the cold on commercial formaldehyde solution (about 40%) in a reflux apparatus yields, first, the compound, $OH\cdot CH_2Cl$. If the action is prolonged, a heavy liquid separates having a composition corresponding with the formula $O(CH_2Cl)_2$. Treatment of this liquid at about 5° with a mixture of concentrated nitric and sulphuric acids results in liberation of hydrogen chloride, carbonyl chloride, and probably an oxygenated chlorine acid, and in separation of a colourless oil, D^4 1·52206, which, from its composition and its cryoscopic behaviour in benzene, appears to have the formula $C_2H_4O_6N_2$. This compound is extremely sensitive to shock, decomposing with detonation. Of the two possible constitutions, $NO\cdot O\cdot CH_2\cdot O\cdot CH_2\cdot O\cdot NO_2$ and $NO_2\cdot CH_2\cdot O\cdot CH_2\cdot O\cdot NO_2$, the latter is the more probable, since hydrolysis leads to the formation of formic

acid and nitromethane. The compound dissolves considerable proportions of cellulose nitrate even at 0°, and an explosive jelly containing 7% of cellulose nitrate (12·11% N) gives a greater increase in volume on explosion than one containing 7% of glyceryl nitrate.

T. H. P.

γ-**Hydroxyvaleraldehyde.** BURCKHARDT HELFERICH (*Ber.*, 1919, **52**, [*B*], 1123—1131).—Although α- and β-hydroxy-aldehydes of simple structure have been closely examined, the corresponding γ-derivatives do not appear to have been isolated, although their chemistry is exceptionally important owing to their near relationship to the sugars. The present communication describes an effort to fill this gap.

A solution of methylheptenol in glacial acetic acid is ozonised, diluted with ether and a little water, and treated with zinc dust until the perozonide is reduced; on distillation, a 78% yield of γ-*hydroxyvaleraldehyde* is obtained. It is a moderately mobile liquid with an odour resembling that of turpentine, b. p. 63—65°/ 10 mm., D_4^{17} 1·0167, n_D^{17} 1·4359, which mixes with water and organic solvents, but is salted out from its aqueous solution by potassium carbonate, but not by sodium sulphate or chloride. The freshly prepared solution contains the aldehyde in the unimolecular form. The *oxime, phenylhydrazone,* and p-*nitrophenylhydrazone* could only be obtained as oils, but the p-*bromophenylhydrazone* forms pale brown crystals, m. p. 88—89° (corr.), after softening at about 85°, and *diphenylmethanedimethyldihydrazone* consists of colourless crystals, m. p. 84—85° (corr.), after slight softening from 80°. The aldehyde yields a *bisulphite* compound, which is readily soluble in water. It does not reduce Fehling's solution in the cold and with only moderate rapidity on heating; ammoniacal silver solution is reduced in the cold. It is converted by concentrated aqueous sodium hydroxide into a crystalline mass, which is transformed into a dark terpinaceous oil when heated. Concentrated hydrochloric acid resinifies the aldehyde slowly in the cold, rapidly when warmed. Treatment of the aldehyde with 1% methyl-alcoholic hydrochloric acid at the ordinary temperature converts it into 5-*methoxy-2-methyltetrahydrofuran,* $\begin{array}{c}CH_2\text{---}CHMe\\CH_2\cdot CH(OMe)\end{array}\!\!>\!O$, a mobile, volatile liquid, b. p. 116—118° (corr.)/755 mm., D_4^{18} 0·9291, n_D^{18} 1·4110, which does not reduce boiling Fehling's solution and only reacts slowly with boiling ammoniacal silver solution. It is stable towards hot alkali and only slowly hydrolysed by hot acid. It does not appear to be hydrolysed by emulsin. When boiled with acetic anhydride, the aldehyde gives 5-*acetoxy-2-methyltetrahydrofuran*, mobile liquid, b. p. 73—78°/9 mm., $D_4^{18\cdot2}$ 1·037, $n_D^{18\cdot2}$ 1·4278, which is gradually converted by water at the ordinary temperature into acetic acid and the aldehyde.

H. W.

Preparation of Xylose from Maize Cobs. K. P. MONROE (*J. Amer. Chem. Soc.*, 1919, **41**, 1002—1003).—The method

described by La Forge and Hudson (*J. Ind. Eng. Chem.*, 1918, **10**, 925) is modified by removing the gum by digestion of the broken maize cobs with sodium hydroxide solution (1%) at 100° for one and a-half hours instead of performing the operation in an auto-clave at 160°; the residue is hydrolysed by dilute sulphuric acid (4%), and the latter is subsequently removed with barium carbon-ate. The sugar solution thus obtained is less coloured than that prepared by previous methods, and crystallisation of the xylose takes place with uniform readiness. The yield is 8—10%. [See also, *J. Soc. Chem. Ind.*, 1919, August.]   H. W.

New Sugar Isolated from a Sea-weed. EIJI TAKAHASHI (*J. Tokyo Chem. Soc.*, 1919, **40**, 157—166).—The author has iso-lated a new sugar from the hydrolytic product of the mucilaginous substance formed by boiling seaweed in water. The sugar crystal-lises from water in rectangular form, thicker in the middle, is exceedingly sweet, is soluble in alcohol, and has m. p. 152—153° and $[\alpha]_D^{20} + 80.75°$. The molecular weight by the cryoscopic method is 179·3. Tests with resorcinol, phloroglucinol, Tollen's and Oshima's reagents show that it is not a ketose, pentose, or methyl-pentose. It yields lævulic acid, identified as the silver salt, and is thus shown to be a hexose. It strongly reduces Fehling's solution, is fermented by yeast, but not so readily as dextrose, and forms a *hydrazone* in the cold, m. p. 158—160°, which is soluble in methyl and ethyl alcohols and in hot water. The needle-shaped *osazone*, m. p. 193°, is soluble in the two alcohols, but not in water. The *phenylmethylhydrazone*, rectangular plates, has m. p. 191°, and the *p-bromophenylhydrazone*, m. p. 171—172°. Sodium amalgam reduces it to a hexahydric *alcohol*, prisms, m. p. 186—187°. The new sugar is very similar to galactose in specific rotatory power and in the m. p. of the corresponding alcohol, but differs in crystalline form, in failure to yield mucic and saccharic acids by oxidation with nitric acid, and in the m. p.'s of the various hydrazones and in the solubility of the osazone in methyl alcohol. From these analyses the author believes the new sugar to be an aldohexose, and names it *floridose*, and its alcohol, *floriditol*. This name is given because the sugar was first isolated from the red sea-weed *Florideae*. Sugars isolated from various sea-weeds, including *Chondrus elatus Holms, Ahnfeltia pricata*, and *Iridaea laminalioidesvar. ornucopiae*, are all easily crystallisable and are found to be absolutely identical with floridose.   CHEMICAL ABSTRACTS.

The Preparation of Rhamnose. E. P. CLARK (*J. Biol. Chem.*, 1919, **38**, 255—256).—Liquid quercitron extract is hydro-lysed by gently boiling with 3% sulphuric acid for half an hour. After removal of the sulphuric acid as barium sulphate, the material is concentrated to a thin syrup and eight volumes of 95% alcohol are slowly added with constant stirring. The filtrate from this precipitation is evaporated to a thick syrup under diminished pressure and the residue is dissolved in 95% alcohol. On the addi-tion of 2½ volumes of ether, a gummy substance is precipitated.

which is redissolved in alcohol and again precipitated by ether. From the extracts, on removal of the ether and concentration, rhamnose may be crystallised out. The yield is 50—51 grams of white rhamnose from 2 kilos. of the commercial quercitron extract.

J. C. D.

The Constitution of the Disaccharides. Part III. Maltose. WALTER NORMAN HAWORTH and GRACE CUMMING LEITCH (T., 1919, **115**, 809—817).

Improvements Relating to the Preparation of Amines. WILLIAM RINTOUL, JOHN THOMAS, and NOBEL'S EXPLOSIVES Co., LTD. (Brit. Pat., 127740).—Tertiary amines are separated from admixture with primary and secondary amines by converting the latter into the corresponding urethanes by treatment with ethyl chloroformate in the cold in presence of aqueous sodium carbonate. The unchanged tertiary base is removed from the residual, oily product by washing with dilute mineral acid, and is recovered by treatment of the acid washings with alkali, whilst the primary and secondary bases are regenerated by the hydrolysis of the urethanes. [See, further, *J. Soc. Chem. Ind.*, 1919, August.]   G. F. M.

Polypeptides containing Glutamine and the Question of the Occurrence in Proteins. H. THIERFELDER and E. von CRAMM [with ALFRED WALTHER] (*Zeitsch. physiol. Chem.*, 1919, **105**, 58—82).—It has been suggested that glutamine and aspara- gine are components of protein rather than glutamic and aspartic acids (Osborne and Gilbert, A., 1906, i, 324; Osborne, Leavenworth, and Braunlecht, A., 1909, i, 72).

A study of the formation of ammonia during the acid hydrolysis of gliadin, polypeptides containing glutamine, and glutamine itself leads the authors to support the view that glutamine is a component of the protein molecule.

The preparation of four dipeptides and of one tripeptide contain- ing glutamine is described.

Chloroacetyl-d-glutamine, $C_7H_{11}O_4N_2Cl$, fine needles from ethyl acetate, m. p. 130—132°, $[\alpha]_D^{18} = -10\cdot33$ to $-10\cdot45°$.

Glycyl-d-glutamine, $C_7H_{13}O_4N_3$, crystallises with one molecule of water, and decomposes at 199—200°, $[\alpha]_D^{18} = -2\cdot47°$. This dipeptide has an acid reaction. It is precipitated by phosphotungstic acid, but is soluble in excess, and gives no biuret test.

Chloroacetyl-d-glutaminylglycine ethyl ester, $C_{11}H_{18}O_5N_3Cl$, needles, m. p. 198°. *Chloroacetyl-d-glutaminylglycine*,

$$C_9H_{14}O_5N_3Cl,$$

needles, m. p. 162—163°. *Glycyl-d-glutaminylglycine*, $C_9H_{16}O_5N_3$, needles, decomposes at 201°, $[\alpha]_D^{19} = -28\cdot4°$. This tripeptide possesses an acid reaction, and is precipitated by phosphotungstic acid, but the precipitate is soluble in an excess of the reagent. It is not pre- cipitated by mercuric chloride, tannic acid, phosphomolybdic acid, basic lead acetate, or saturated ammonium sulphate solution. It gives a bluish-violet biuret reaction.

d-α-*Bromopropionyl*-d-*glutamine*, $C_8H_{13}O_4N_2Br$, m. p. 156—157°, $[a]_D^{19} = +9.03—9.3°$. d-*Alanyl*-d-*glutamine*, $C_8H_{15}O_4N_3$, prisms, m. p. 222° (decomp.), $[a]_D^{18} = -9.2°$. It possesses an acid reaction to litmus and gives no biuret test.

l-α-*Bromopropionyl*-d-*glutamine*, $C_8H_{13}O_4N_2Br$, rosettes of needles, m. p. 132°. When recrystallised from ethyl acetate the substance gave a rotation in methyl alcohol of $[a]_D^{18} = -17.42°$. The substance, recrystallised from water, gave in the same concentration $[a]_D = -16.4°$. No explanation is put forward. l-*Alanyl*-d-*glutamine*, $C_8H_{15}O_4N_3$, needles, m. p. 212—213°, $[a]_D^{15} = -20.1°$. This substance is acid to litmus and gives no biuret reaction.

d-α-*Bromoisohexoyl*-d-*glutamine*, $C_{11}H_{19}O_4N_2Br$, m. p. 150°, $[a]_D^{19} = +20.8°$, $[a]_D^{25} = +20.55°$, crystallises in prisms. l-*Leucyl*-d-*glutamine*, $C_{11}H_{21}O_4N_3$, needles, m. p. 235—236°, $[a]_D^{18} = +12.6°$. It is acid to litmus and gives no biuret reaction. J. C. D.

Catalytic Action of Hydrogen Peroxide on Potassium Ferro- and Ferri-cyanides. E. LÜCK (*Apoth. Zeit.*, 1919, **34**, 87 ; from *Chem. Zentr.*, 1919, i, 610—611).—If an aqueous solution of potassium ferricyanide is warmed for about two minutes at 45° with 10% of hydrogen peroxide and allowed to cool, almost black *crystals*, $2K_3FeC_6N_6,3H_2O_2$, are obtained which are very sparingly soluble in water, mol. wt. 759.82. In a similar manner, potassium ferrocyanide gives the *compound*, $2K_4FeC_6N_6.3H_2O_3$. H. W.

Modified Graphic Formulæ for Organic Cyclic Compounds. ALEXANDER LOWY (*J. Amer. Chem. Soc.*, 1919, **41**, 1029—1030).— The author recommends the advisability of indicating the double bonds in cyclic compounds by heavy lines and the single bonds by light lines. A series of typical examples is given. H. W.

Freezing-point Curves of Mixtures of Nitro- and Dinitro-benzene. K. LEHMSTEDT (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1918, **13**, 118—119; from *Chem. Zentr.*, 1919, i, 708).—The author has determined the freezing point of various solutions of pure n-dinitrobenzene and of a mixture of o-, m-, and p-dinitrobenzene (6.5%, 92.0%, and 1.5% respectively) in nitrobenzene. The composition of nitrated products can be readily elucidated from the freezing-point curve for the pure dinitrobenzene and for the technical mixture of isomerides. The curve has two eutectic points, probably due to the fact that solutions which contain little dinitrobenzene are not caused to crystallise by seeding with dinitrobenzene. H. W.

The Reduction of 2 : 3-, 3 : 4-, and 2 : 5-Dinitrotoluenes. JAKOB MEISENHEIMER and ERICH HESSE (*Ber.*, 1919, **52**, [*B*], 1161—1177).—Some years ago (A., 1904, i, 150; 1906, i, 642) it was shown that o- and p-dinitrobenzenes are converted by cautious reduction in alkaline solution into dark-coloured salts of *diaci-dinitrocyclo*hexadienes, which, when acidified, rapidly pass into

nitronitrosobenzenes. The experiments with o-dinitrobenzene have been repeated on a large scale, the products now obtained being o-nitronitrosobenzene (19% of that theoretically possible), nitro-benzene (31%), o-nitrophenol (14%), a little o-nitroaniline, and resinous matter.

The work has also been extended to 2:3-, 3:4-, and 2:5-dinitro-toluenes, which are found to behave in a precisely similar manner.

3:4-Dinitrotoluene, m. p. 59—60°, is conveniently prepared by oxidising 3-nitro-p-toluidine by means of·Caro's acid to 3-nitro-4-nitrosotoluene, and completing the oxidation of the latter with nitric acid. Reduction of 3:4-dinitrotoluene by hydroxylamine is effected in the usual manner, but the salt which is produced cannot be isolated on account of its ready solubility. On acidification, the following substances are obtained: 3-nitro-4-nitrosotoluene, m. p. 143°; 4-nitro-3-nitrosotoluene, yellow leaflets, m. p. 141°; a mixture of m- and p-nitrotoluenes, p-nitro-m-cresol, m. p. 56°, and resinous products, from which nothing definite could be isolated . *Potassium diaci*-3:4-*dinitromethyl*-$\Delta^{1·5}$-*cyclohexadiene* is prepared by the addition of an ethereal solution of potassium ethoxide to a suspension of 3-nitro-4-nitrosotoluene in ether, and forms an amorphous powder of dark red colour which is extraordinarily sensitive to moisture; when treated with aqueous acid, it yields a mixture of nitronitrosotoluenes.

2:3-Dinitrotoluene, m. p. 96—97°, is best obtained by the nitra-tion of acet-o-toluide by nitric acid in the presence of acetic acid, and decomposition of the mixture of 3- and 5-nitroacet-o-toluides with hydrochloric acid; the separation of the isomeric amines is accomplished by diluting the acid solution largely with water, when the very feebly basic 3-nitro-o-toluidine is precipitated; the latter is converted by Caro's acid into 3-*nitro*-2-*nitrosotoluene*, pale yellow leaflets, m. p. 126—127° (decomp.), which is transformed by nitric acid into 2:3-dinitrotoluene. (6-*Nitro*-2:4'-*dimethylazobenzene* red prisms, m. p. 65·5—66°, is obtained by condensing 3-nitro-nitrosotoluene with p-toluidine in glacial acetic acid solution; if aniline is used, 6-*nitro*-2-*methylazobenzene* is obtained as a red oil b. p. 215°/11 mm., which does not solidify after many months. Reduction of 2:3-dinitrotoluene with hydroxylamine follows the normal course, yielding 2-*nitro*-3-*nitrosotoluene*, yellow leaflets m. p. 92—93°, a mixture of o- and m-nitrotoluenes, and 3-nitro-o-cresol, m. p.·69—70°. The *potassium* salt of diaci-2:3-dinitro-methyl-$\Delta^{4·6}$-*cyclo*hexadiene is prepared from 3-nitro-2-nitroso-toluene, and is very sensitive to moisture.

5-*Nitro*-2-*nitrosotoluene*, almost colourless crystals, m. p. 143—144°, is obtained by the action of Caro's acid on the corre-sponding amine (it condenses with aniline to yield 4-*nitro*-2-*methyl*-*azobenzene*, red prisms, m. p. 98—99°), and is readily trans-formed into 2:5-dinitrotoluene, m. p.·50—51°. The latter is reduced by hydroxylamine, and the solution yields on acidification 5-nitro-2-nitrosotoluene and *dinitroazoxytoluene*, dark brown prisms, m. p. 188—189°. The *potassium* salt of *diaci*-2:5-*dinitro*-

methyl-Δ³·⁶-cyclohexadiene is obtained as with the other isomerides, and forms an unstable, red salt, which, when acidified, gives dinitro-azoxytoluene. When reduction of 2:5-dinitrotoluene by hydroxylamine is effected in highly concentrated solution, *potassium nitro-toluene*iso*diazotate*, $C_7H_6O_3N_3K,H_2O$, is precipitated in yellow needles, m. p. 202° (decomp.); the substance owes its origin to the action oʰ hydroxylamine on the intermediately formed nitroso-derivative, $NO_2 \cdot C_6H_3Me \cdot NO + NH_2 \cdot OH + KOH =$

$$NO_2 \cdot C_6H_3Me \cdot N \vdots N \cdot OK + 2H_2O,$$
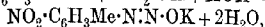
as is shown by its formation by the interaction of hydroxylamine with 5-nitro-2-nitrosotoluene. Attempts are also described to prepare it by the diazotisation of 5-nitro-*o*-toluidine and treatment of the product with sodium hydroxide solution, but the yellow, crystalline material exploded with great violence. H. W.

Preparation of Liquid Hydrocarbons by the Action of Aluminium Chloride on Naphthalene under Pressure.

FRANZ FISCHER (*Ges. Abhand. Kennt. Kohle*, 1917, **1**, 237—244; from *Chem. Zentr.*, 1917, ii, 584).—[With WILHELM SCHNEIDER.]— A mixture of naphthalene (100 grams) and powdered aluminium chloride (4 grams), when boiled under reflux during three hours and subsequently distilled, yielded about 47 grams of naphthalene impregnated with oil and a residue of 47 grams of a brittle pitch which, when heated to redness, gave a small amount of viscous distillate and much coke. On the other hand, when naphthalene (250 grams) and aluminium chloride (10 grams) were heated under pressure (up to ten atmospheres) at 330° during twenty minutes, 124·5 grams of oil containing naphthalene and 108 grams of charred matter were obtained, from which 92 grams of non-solidifying oil were isolated by freezing and pressing. It is therefore possible to convert technically pure naphthalene by 4% of aluminium chloride in autoclaves into a mixture of liquid hydrocarbons, the yield of which is 40%; the remainder of the naphthalene is converted into a mixture of pitch and carbon, since a portion of the naphthalene is hydrogenated at the expense of the other portion.

[With SIEGFRIED HILPERT.]—1055 Grams of non-solidifying oil were obtained from 3250 grams of naphthalene and 130 grams of aluminium chloride; after treatment with calcium oxide to remove hydrogen chloride, the oil was distilled, and yielded 4% b. p. below 150°, 79% b. p. 150—300°, and 16% residue of higher b. p. The chief fraction, when cooled to 0°, deposited 27% of its weight of naphthalene, so that the remainder, which had b. p. 150—300° and did not solidify at 0°, constituted 57% of the total oil, or 18% of the original naphthalene. The middle fraction contained 8·4% of hydrogen and 91·5% of carbon. Its heat of combustion was 9932 Cal. (naphthalene, 9628 Cal.; dihydronaphthalene, 10,092 Cal.). The viscosity in Engler's apparatus was 1·16 at 20° and the flash point 70° (Pensky Martens), 75° (open test). The hydrogenated naphthalene could not be burnt in ordinary petroleum lamps without formation of soot. H. W.

Preparation of Thickening Material for Lubricating Oils from Naphthalene. FRANZ FISCHER (*Ges. Abhand. Kennt. Kohle*, 1917, **1**, 254; from *Chem. Zentr.*, 1919, ii, 584).— Complex compounds, formed by the condensing action of aluminium chloride, remain undecomposed when naphthalene and aluminium chloride are heated at a moderate temperature (compare preceding abstract). Thus, when crude naphthalene (500 grams) is heated in an autoclave with aluminium chloride (50 grams) (the maximum temperature and pressure being respectively 55° and two atmospheres) and the product is distilled with steam, a black, syrupy, viscous residue remains which, after being filtered through cloth while hot, gives with three parts of a fatty tar oil, a black lubricating oil of good quality.   II. W.

Conversion of Naphthalene into Liquid Products. HERMANN NIGGEMANN (*Ges. Abhand. Kennt. Kohle*, 1917, **1**, 255—258; from *Chem. Zentr.*, 1919, ii, 584—585. Compare preceding abstracts). —Attempts have been made to methylate naphthalene by heating it with polymethylbenzenes in the presence of aluminium chloride, since this substance not infrequently causes a wandering of the methyl groups in methylbenzenes. When xylene, b. p. 134—135°, was heated to boiling with aluminium chloride for three hours, a mobile, dark brown, and a viscous, black oil were obtained from the former, of which fractions boiling below and above xylene were isolated. Noticeable action did not occur when dry hydrogen chloride was passed through a suspension of dry aluminium hydroxide in xylene. Under similar conditions, solvent naphtha (25 grams, b. p. 150—175°) yielded fractions, b. p.'s 145—150° (2 grams), 150—175° (15 grams), 175—205° (3 grams), whilst the residue after decomposition with hydrochloric acid gave 2 grams, b. p. 150—280°. A mixture of naphthalene and xylene yielded an oil, b. p. 125—220°, which partly solidified, whilst a mixture of naphthalene and solvent naphtha gave small fractions, b. p.'s 110—150° and 150—175°, and a larger fraction, b. p. 175—225°, consisting of naphthalene impregnated with oil. When naphthalene was boiled with aluminium chloride (4%) during one and a-half hours, and the product treated with hot dilute hydrogen chloride and distilled, oily naphthalene was obtained at 210—225°, and a substance, which solidified to a yellow, waxy mass when the distillation was continued to 220° in an absolute vacuum.

Acenaphthene when boiled with aluminium chloride (4%) for one and a-half hours yielded a yellowish-green, fluorescent oil, b. p. 195—265°, which remained liquid at the ordinary temperature, but deposited acenaphthene at 0°. Similarly, anthracene gave an oil, b. p. 200—300°, which formed a mass of orange crystals at the ordinary temperature, whilst phenanthrene yielded a yellowish-green, fluorescent oil, which partly solidified at 0° and became liquid again at the ordinary temperature.   H. W.

Conversion of Naphthalene into Liquid Products by Alkylation.

FRANZ FISCHER and WILHELM SCHNEIDER (*Ges. Abhand. Kennt. Kohle*, 1917, **1**, 227--230; from *Chem. Zentr.*, 1919, ii, 585. Compare preceding abstracts).--The object of the investigation was the technical liquefaction of naphthalene by alkylation in the simplest possible manner. Naphthalene (5 grams) when heated with absolute alcohol (4·5 c.c.) and zinc chloride (10 grams) at 290--300° during thirty-six hours yielded 0·2 gram of recovered naphthalene and 5·1 grams of a reddish-brown oil with a green fluorescence. By treatment of crude naphthalene (100 grams) with alcohol (96%, 120 c.c.) and zinc chloride (200 grams regenerated, 200 grams fresh substance) at 180--190° during sixty hours it gave 112 grams of a dark brown oil with a green fluorescence which, on distillation, yielded a small fraction, b. p. below 240°, 98 grams of a volatile, yellow oil, b. p. 240--300°, and 12 grams of dark brown, viscous, residual oil; naphthalene did not separate from these oils when cooled with ice-water. The zinc chloride cannot be replaced by granulated calcium chloride, sulphuric acid, sodium hydrogen sulphate, or anhydrous magnesium chloride. When naphthalene (5 grams) was heated with methyl alcohol (3·3 c.c.) and zinc chloride (10 grams) at 290--300° during twelve hours, 3·8 grams of oil were obtained, together with 0·8 gram of naphthalene. A mixture of naphthalene and phenol when heated with zinc chloride at 290--300° gave a considerable amount of carbon and large amounts of unchanged substances. Acetone appeared to react with naphthalene in the presence of zinc chloride with elimination of water. Acetylene and ethylene did not react with naphthalene at 100--200° in the presence of aluminium chloride.　　　　　　　　　　　　　　　　　　　　H. W.

Conversion of Naphthalene into Liquid Products by Hydrogenation in Pressure Furnaces in the Presence of Non-metallic Catalysts.

FRANZ FISCHER and HERMANN NIGGEMANN (*Ges. Abhand. Kennt. Kohle*, 1917, **1**, 231--236; from *Chem. Zentr.*, 1919, ii, 585--586). -The experiments were performed in an electrically heated, horizontal furnace capable of withstanding high pressures. Naphthalene was found to be very resistant to high temperatures, and, except for slight discoloration and traces of separation of carbon, remained unchanged when heated during one hour at 500° in the presence or absence of copper, iron, coke, or selenium; in the presence of 1% of iodine, it became intensely black, owing to separation of carbon. The best conditions for obtaining liquid products from naphthalene by hydrogenation consist in employing high temperatures and pressures. In the absence of catalysts or in the presence of selenium, the liquefaction is minimal. Iodine, on the other hand, is an active catalyst; naphthalene is completely liquefied by heating with 1% of iodine at 550° for one hour in an atmosphere of hydrogen (pressure to about 170 atmospheres) to an oil with a

blue fluorescence, a mirror of carbon being also formed. Carbonisation occurs more readily at high than at low pressures; separation of carbon at a hydrogen pressure less than 50 atmospheres does not occur below 800°, with 50 atmospheres at 800°, with 100 atmospheres at 550°, with 170 atmospheres below 550°. The hydrogenated oils solidify more or less completely after a few days, probably owing to oxidation and separation of dissolved naphthalene.   H. W.

Constitution of certain Polynitro-compounds. J. BISHOP TINGLE and WALTER ALBERT LAWRANCE (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 7—11).—The authors have determined the constitution of the nitration products of picranilide and diphenylamine obtained by Tingle and Blanck (compare A., 1908, i, 778), and shown by Tingle and Burke to be tetranitrodiphenylamines (compare A., 1910, i, 21). By the action of nitric acid on picranilide in the presence of oxalic acid, the product obtained is 2:4:6:4'-tetranitrodiphenylamine, m. p. 216°. By the action of trichloroacetic and nitric acids, picranilide yields s-tetranitrodiphenylamine, m. p. 191°, together with some bis-2:4-tetranitrodiphenylamine, m. p. 179—180°. On nitrating diphenylamine itself, three compounds are obtained, namely, s-tetranitrodiphenylamine as the main product, together with a small quantity of a *tetranitrodiphenylamine*, m. p. above 250°, and a *compound*, not identified.   W. G.

Salts of Hexanitrodiphenylamine. H. KAST and A. LANGHANS (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1919, **14**, 1—4, 25—27; from *Chem. Zentr.*, 1919, i, 719).—The acidic character of hexanitrodiphenylamine, due to the presence of the imide-hydrogen atom, enables it to form soluble salts of orange-yellow to blood-red colour. Readiness of salt formation is considerably restricted by the sparing solubility of the parent substance. A series of salts has, however, been prepared by agitating and warming an aqueous or alcoholic solution or suspension of the requisite metallic oxides, hydroxides, or carbonates with hexanitrodiphenylamine. The *magnesium* salt is the most readily soluble, and may conveniently be used in obtaining the salts of the heavy metals by double decomposition. The salts, with the exception of those of magnesium and *ammonium*, are more sensitive than the parent substance. The lead salt is the most sensitive, followed in order by the copper, sodium, iron, potassium, calcium, and ammonium salts. The sequence, with the exception of the sodium salt, is therefore the same as with the salts of picric acid and trinitro-cresol.   H. W.

Preparation of Hexanitrodiphenylamine from Chloro-benzene. E. J. HOFFMAN and PERRY A. DAME (*J. Amer. Chem. Soc.*, 1919, **41**, 1013—1020).—The preparation is effected in the following stages; (i) nitration of chlorobenzene to chlorodinitro-

benzene by a mixture of nitric and sulphuric acids, (ii) formation of dinitrodiphenylamine by heating chlorodinitrobenzene with aniline, (iii) preparation of tetranitrodiphenylamine by the action of nitric acid on the dinitro-compound (compare Carter, *Zeitsch. ges. Schiess. Sprengs.*, 1913, **8**, 205, 251), and (iv) conversion of tetranitrodiphenylamine into hexanitrodiphenylamine by nitric-sulphuric acid, the latter procedure being a modification of Carter's method. The best experimental conditions for each stage are fully described, and the yield of hexanitro-derivative is 68·62% of that theoretically possible, calculated on the basis of chlorobenzene used. The authors' results lead them to the conclusion that the intermediate isolation of the tetranitro-compound is probably unnecessary, and that the dinitro- can be converted directly into the hexanitro-derivative. The latter crystallises in fine, yellow needles, m. p. 240—250° (decomp.). It is a very brisant explosive, scarcely suitable for explosive purposes except when mixed with other substances. It is much more poisonous than glyceryl nitrate, and causes severe blisters, resembling burns, when it comes in contact with the skin. The fine dust especially affects destructively the mucous membranes of the mouth, nose, and lungs.   H. W.

Catalytic Hydrogenation of Schiff's Bases. ALPH. MAILHE (*Bull. Soc. chim.*, 1919, [iv], **25**, 321—325).—Schiff's bases, obtained by condensing an aldehyde with a primary amine, readily undergo hydrogenation when passed with hydrogen over reduced nickel at 200—230°, giving the corresponding secondary amine. At the same time, there is a slight secondary reaction, represented by the equation $R \cdot CH \colon NR' + 2H_2 = R \cdot CH_3 + R' \cdot NH_2$. Satisfactory yields were obtained in this manner from five of these bases.   W. G.

N-Phenylhydroxylamine and Methyl Sulphate. EUG. BAMBERGER and ALEXANDER LANDAU (*Ber.*, 1919, **52**, [*B*], 1093—1110).—Since previous attempts to prepare alkyl derivatives of N-phenylhydroxylamine by means of methyl iodide, methyl bromide, or diazomethane did not give the desired result, the authors have examined the action of methyl sulphate without, however, being able to effect the isolation of the ethers.

The majority of the experiments were performed by adding methyl sulphate and sodium hydrogen carbonate to an aqueous solution or suspension of phenylhydroxylamine at 0°. In these circumstances the most readily isolable product is the methylenediphenylhydroxylamine, $CH_2(NPh \cdot OH)_2$, which had previously been obtained by the use of diazomethane as methylating agent (Bamberger and Tschirner, A., 1900, i, 342). In addition, small quantities of azoxybenzene, aniline, and mono- and di-methyl-anilines were isolated, but it is uncertain whether the latter were produced by the methylation of aniline or by the decomposition of phenylmethylhydroxylamine. The methylene-diphenylhydroxylamine was accompanied by a second base which was without doubt formed from it during its purification, and which was identified as glyoxime-N-phenyl ether, $O \colon NPh \colon CH - CH \colon NPh \colon O$. Small amounts

of oily and crystalline substances were also produced, but in quantity scarcely sufficient for complete identification. Among these was a substance crystallising in colourless leaflets, m. p. about 132° (which closely resembled diphenyl-N-hydroxyformamidine,

$$OH \cdot NPh \cdot CH\dbond NPh,$$
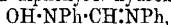
but complete identity could not be established), a product, m. p. 232°, and an impure oil which possibly contained phenylmethyl-hydroxylamine. Since the total weight of these products did not correspond with the amount of material employed, the residual aqueous solution was treated with sulphuric acid and sodium nitrite, when p-nitrodimethylaniline, m. p. 162°, and o-nitrodimethylaniline were obtained. The only probable source of these substances was dimethylaniline N-oxide, which was actually isolated in the form of its picrate; it is remarkable that the amount of the latter generally appears to increase when the reaction mixture is preserved.

When phenylhydroxylamine and methyl sulphate were mixed, the reaction became extremely violent after a short time; in the presence of ether as diluent, the action could be conveniently regulated and the products were dimethylaniline oxide, methylenedi-phenyl-hydroxylamine, small quantities of aniline, and the methylanilines and substances of unknown composition. A portion of the phenyl-hydroxylamine was removed from action in the form of its methosulphate. In addition, a reddish-brown oil was obtained which possibly contains phenylhydroxylamine O-methyl ether.

Attempts were also made to use nascent phenylhydroxylamine by reducing nitrobenzene with zinc and ammonium chloride in the presence of methyl sulphate; the products, however, were the same as those obtained previously.

The production of methylenedi-phenylhydroxylamine during the methylation of phenylhydroxylamine is explained in the following manner: the primary product of the change is phenylmethylhydroxylamine, which spontaneously decomposes into formaldehyde and aniline, $Ph \cdot NMe \cdot OH = CH_2O + PhNH_2$; the formaldehyde then condenses with more phenylhydroxylamine to yield methylenedi-phenylhydroxylamine. The conversion of the latter by boiling water or alcohol into glyoxime-N-phenyl ether depends on its hydrolysis to formaldehyde and N-phenylhydroxylamine and reaction between these substances: $OH \cdot NPh \cdot CH_2 \cdot NPh \cdot OH + H_2O = CH_2O + 2NHPh \cdot OH$ and $2CH_2O + 2NHPh \cdot OH = O\dbond NPh \cdot CH \cdot CH\dbond NPh\dbond O + 2H_2O + H_2$. In an intermediate stage the formaldehyde condenses under the basic influence of phenylhydroxylamine to glycollalde-

hyde, which reacts thus: $OH \cdot CH_2 \cdot CHO \xrightarrow{\quad\overset{NHPhOH}{}\quad} OH \cdot NPh \cdot CH_2 \cdot CHO$

or $OH \cdot NPh \cdot CH_2 \cdot CH\dbond NPh\dbond O \longrightarrow O\dbond NPh\dbond CH \cdot CH\dbond NPh\dbond O + H_2$. The liberated hydrogen is used in the reduction of a further molecule of phenylhydroxylamine.   H. W.

Attempts to Prepare β-Phenylhydroxylamine O-Methyl Ether. Eug. Bamberger (*Ber.*, 1919, **52**, [*B*], 1111—1123).— Attempts to prepare the substance by the action of methyl iodide or

methyl bromide under widely varied conditions did not lead to the desired result, the products generally consisting of azoxybenzene, azobenzene, aniline, and methylaniline. Similarly, the product could not be obtained by the hydrolysis of *N*-benzoylphenylhydroxyl-amine *O*-methyl ether or of phenyloxyurethane *O*-methyl ether. Apparently, phenylhydroxylamine *O*-methyl ether dissociates with extreme readiness under the influence of hydroxyl ions into PhN< (or azobenzene) and methyl alcohol.

[With K. Blaskopf and Alexander Landau.]—*N*-Benzoylphenyl-hydroxylamine and dibenzoylphenylhydroxylamine are prepared by the action of benzoyl chloride on an aqueous solution of phenyl-hydroxylamine in the presence of sodium hydrogen carbonate or sodium acetate, and are conveniently separated by taking advantage of the solubility of the former and insolubility of the latter in aqueous ammonia; they form colourless needles, m. p. 121–122°, and shining needles, m. p. 117—118° respectively. N-*Benzoyl-phenylhydroxylamine* O-*methyl ether*, cubic crystals, m. p. 54·5—55°, is prepared by the action of methyl iodide and sodium methoxide on the mono-benzoyl compound or, more conveniently, by the methyl sulphate method. When hydrolysed with boiling methyl-alcoholic potassium hydroxide, it yields azobenzene; with aqueous alkali in the presence of acetone, it gives benzoic acid, azo-benzene, aniline, and, possibly, *p*-anisidine; with aqueous alkali the chief products are benzoic acid and azobenzene. Benzoic acid, *p*-aminophenol, aniline, and *p*-anisidine are formed when sulphuric acid and methyl alcohol are used, whilst when the latter is replaced by ethyl alcohol *p*-phenetidine is produced.

[With F. Tschirner.]—*Hydroxyphenylurethane*,

$$NPh(OH)\cdot CO_2Et,$$
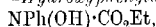
colourless, silky prisms, m. p. 47·5°, is prepared by the action of ethyl chloroformate on an ethereal solution of phenylhydroxylamine (the *sodium* derivative forms fine, colourless crystals), and is reduced by zinc dust and acetic acid to phenylurethane, m. p. 51°. m-*Tolyl-hydroxyurethane* is similarly prepared and has m. p. 30°. When treated with methyl iodide and potassium methoxide, phenyl-hydroxyurethane is converted into *methoxyphenylurethane*, mobile oil, b. p. 124°/12 mm. The latter is hydrolysed by aqueous ammonia, yielding, as main products, ethylurethane and azobenzene.

H. W.

Preparation of Acyl Derivatives of a *p*-**Aminophenyl Ether.** Gesellschaft für Chemische Industrie in Basel (D.R.-P. 310967; from *Chem. Zentr.*, 1919, ii, 422—423).—*p*-Aminophenyl allyl ether is caused to react with aliphatic acids, acid anhydrides, or acid haloids if necessary in the presence of a suitable diluent or condensing agent. p-*Acetylaminophenyl allyl ether*, shining leaflets, m. p. 94°, is thus obtained by boiling the amino-ether with acetic anhydride. *Lactylaminophenyl allyl ether*, from the amino-ether and lactide at 150°, forms shining leaflets, m. p. 87°. iso*Valeryl-p-aminophenyl allyl ether*, small needles, m. p. 95°, is obtained from the acid, whilst *a-bromoisovaleryl-p-aminophenyl allyl ether*, shining

leaflets, m. p. 131°, is prepared from the amino-ether and α-bromo-isovaleryl bromide in the presence of ether and sodium carbonate. The substances are powerful soporifics, which also possess sedative and antineuralgic properties.   H. W.

p-Cymene. II. Utilisation of Cymene for the Preparation of Photographic Developers.   HERBERT A. LUBS (*J. Ind. Eng. Chem.*, 1919, **11**, 455—456. Compare Andrews, A., 1918, i, 339).—Cymene is nitrated and the nitro-derivative reduced to 4-*iso*propyl-*o*-toluidine (*ibid.*), which is converted through the diazo-reaction into carvacrol. This is transformed into the *p*-nitroso-compound by adding sodium nitrite to an alcoholic solution of the phenol, saturated with hydrogen chloride, and the product is dissolved in 10% ammonia solution and reduced by hydrogen sulphide, when *p*-aminocarvacrol [Me:Pr:OH:NH₂=1:4:2:5] is precipitated in colourless leaflets. This is a better developer than *p*-aminophenol and gives as good tones as metol, but it does not keep quite so well as this in the developing bath.

Thymoquinol may also be made from sulphonated carvacrol, but the yields are poor and it offers no advantages over quinol. *p*-Aminothymol is also not a suitable developer.   ·J. C. W.

3-Nitro-*o*-toluic Acid.   S. GABRIEL and ARTHUR THIEME (*Ber.*, 1919, **52**, [*B*], 1079—1092).—3-Nitro-*o*-toluic acid, the last of the ten theoretically possible nitrotoluic acids, has been recently described by Mayer (A., 1915, i, 958); the authors find that some · of his data are incorrect, and have re-investigated the substance.

Acet-*o*-toluidide is converted by nitric acid in acetic acid solution in the presence of acetic anhydride into a mixture of 3- and 5-nitro-acet-*o*-toluidides, which are hydrolysed with concentrated hydrochloric acid; under suitable conditions, 3-nitro-*o*-toluidine can be precipitated from this solution by addition of water, whilst the 5-nitro-isomeride remains dissolved. The former is reduced by hydriodic acid to the corresponding diamine, m. p. 63—64°, the relative position of the amino-groups following from its transformation into 4(or 7)-methylbenziminazole, m. p. 145° (*hydrochloride*, rhombic plates which do not melt below 300°). 3-Nitro-*o*-toluonitrile, silvery leaflets, m. p. 109—110°, is prepared by Sandmeyer's method and treatment of the crude product with alcohol or with nitric acid; it is reduced by hydriodic acid and phosphorus to 3-*amino-o-toluo-nitrile*, m. p. 127—128°, which by further application of Sandmeyer's reaction gives 3-*methylphthalonitrile*, colourless needles, m. p. 143°, from which 3-methylphthalimide, m. p. 189—190°, is prepared by the action of sulphuric acid. Attempts to hydrolyse 3-nitro-*o*-toluonitrile directly to the acid were unsuccessful, but it is transformed by sulphuric acid into 3-*nitro-o-toluamide*, delicate needles, m. p. 158°, which is readily converted by Bouveault's method into 3-nitro-*o*-toluic acid, long, colourless needles or short rods, m. p. 151—152° [the *sodium* (+3·5H₂O), *barium* (+3H₂O),

and *silver* salts are described]. The acid cannot be directly esterified by methyl alcohol and hydrogen chloride, but the *methyl* (needles and leaflets, m. p. 50°) and *ethyl* (oily) esters are readily prepared by the action of the requisite alcohol on the acid *chloride*, m. p. 41°. 3-*Nitro-o-toluic anhydride* forms six-sided plates, m. p. 174°.

3-Nitro-*o*-toluamide is converted by prolonged treatment with boiling hydriodic acid into carbon dioxide and *m*-toluidine; when reduced with tin and hydrochloric acid it yields 3-*methylbenziso-oxazole*-3-*one*, slender needles, m. p. 119—120° (decomp.), *m*-toluidine hydrochloride, and 3-*amino-o-toluic acid hydrochloride*; the free *acid*, needles, m. p. 125—126° (decomp.), may also be prepared by reduction of the nitro-acid with ferrous sulphate in ammoniacal solution. When heated with formamide, it is converted into 5-*methylquinazole*-4-*one*, long needles, m. p. 224°.

Ethyl nitrotoluoylmalonate, $C_6H_3Me(NO_2)\cdot CO\cdot CH(CO_2Et)_2$, prisms, m. p. 60°, is prepared by the action of 3-nitro-*o*-toluoyl chloride on ethyl sodiomalonate, and yields a *potassium* derivative, $C_{15}H_{16}O_7NK$, yellow, silky needles. When boiled with hydriodic acid and red phosphorus, it gives 2 : 4-*dihydroxy*-5-*methylquinoline*, microcrystalline powder, which does not melt at 300°, and is converted by phosphoryl chloride into 2 : 4-dichloro-5-methylquinoline, long, slender needles, m. p. 132°. Treatment with tin and fuming hydrochloric acid transforms the dichloro-base into a mixture of 5-*methyltetrahydroquinoline hydrochloride*, needles and leaflets, m. p. 238—240° (the *nitroso*-derivative of the tetrahydro-base crystallises in shining, oblique prisms, m. p. 69—70°), and 5-methylquinoline, b. p. 263—264°/753 mm., 264—265°/765 mm. (picrate, m. p. 218—219°, methiodide, lemon-yellow needles and plates, m. p. 197° after softening at 193°); the latter base can also be obtained in small yield by distilling 2 : 4-dihydroxy-5-methylquinoline with zinc dust.

The following details of previously undescribed nitro- and aminotoluonitriles are given. 5-Nitro-*o*-toluonitrile (compare Mayer, *loc. cit.*), prepared from 5-nitro-*o*-toluidine in the manner used for the 3-isomeride, forms colourless leaflets, m. p. 100°, which are readily hydrolysed by a mixture of glacial acetic and fuming hydrochloric acids at 165°, to 5-nitro-*o*-toluic acid, m. p. 152—153°. The nitro-nitrile is readily reduced by stannous chloride and hydrochloric acid to 5-*amino-o-toluonitrile*, rhombic crystals, m. p. 90°. 6-Nitro-*m*-toluonitrile, m. p. 80°, is similarly reduced to 6-*amino-m-toluonitrile*, long, colourless needles, m. p. 95°. 5-*Nitro*-m-*toluo-nitrile*, needles, m. p. 104—105°, is prepared by the action of thionyl chloride on the corresponding *amide*, small needles, m. p. 164—165° (from 5-nitro-*m*-toluoyl chloride and ammonia in ethereal solution); 5-*amino*-m-*toluonitrile* forms needles, m. p. 75° (the *hydrochloride* is slowly volatile at 100°). 2-Nitro-*m*-toluonitrile, m. p. 84°, is reduced by hydriodic acid or ammonium sulphide to 2-amino-*m*-toluamide, m. p. 149°; by stannous chloride and hydrochloric acid to 2-*amino*-m-*toluonitrile*, m. p. 38°. H. W.

A Novel Application of Bromine Water in Synthetic Organic Chemistry. JOHN READ and MARGARET MARY WILLIAMS (*J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 558—564).— It has previously been shown (T., 1917, **111**, 240) that ethylene reacts directly with bromine water to give a good yield of ethylene bromohydrin. In the same way when air charged with bromine vapour is passed through a suspension of cinnamic acid in ice-cold water kept well stirred, a yield of over 80% of α-bromo-β-phenyl-hydracrylic acid is obtained, the other product being αβ-dibromo-β-phenylpropionic acid. If the cinnamic acid is replaced by sodium cinnamate only 53% of the bromohydrin is obtained, and there is a third product, namely, β-bromostyrene, which accounts for 42·6% of the sodium cinnamate used.   W. G.

Fluorocinnamic Acid. F. SWARTS (*Bull. Soc. chim.*, 1919, [iv], **25**, 325—335).—When benzaldehyde is slowly added to methyl fluoroacetate in the presence of sodium, the mixture being cooled below 0°, the principal product is *methyl fluorocinnamate*, m. p. 25°, b. p. 138°/23 mm., $D^{54·2}$ 1·17258. It is readily saponified by aqueous potassium hydroxide, giving the *potassium* salt, from which, on acidifying, *fluorocinnamic acid*, m. p. 157·6° (corr.), b. p. 290°, is obtained. It yields *calcium*, *barium*, and *silver* salts and two complex *iron* compounds having the composition:

$$[Fe_3(C_9H_6FO_2)_6(OH)_2]C_9H_7FO_2,$$

and

$$\left[O{<}{Fe_3(C_9H_6FO_2)_6(OH) \atop Fe_3(C_9H_6FO_2)_5(OH)_3}\right](C_9H_7FO_2)_2.$$
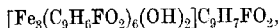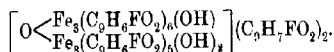
Fluorocinnamic acid is readily brominated, giving *α-fluoro-αβ-dibromo-β-phenylpropionic acid*, m. p. 161·8°, giving a *barium* salt and a *methyl* ester, m. p. 120° (corr.).   W. G.

Action of Ammonia and Amines on the Substituted Carbamides and Urethanes. I. Carbonyldiurethane. F. B. DAINS, H. W. GREIDER, and C. H. KIDWELL (*J. Amer. Chem. Soc.*, 1919, **41**, 1004—1013).—Carbonyldiurethane, silky needles, m. p. 108°, is readily prepared by the addition of urethane (2 mols.) and pyridine (2 mols.) to a 10% solution of carbonyl chloride in benzene. It does not react with anhydrous liquid ammonia, but, in the presence of a little water, it gives carbethoxybiuret, m. p. 162—163°, traces of biuret, and cyanuric acid. No reaction occurs with cold alcoholic ammonia, but with aqueous ammonia (28%) the main reaction consists in the hydrolysis of one of the carbethoxy-groups, with the resulting production of ethyl allophanate, m. p. 192° (the *silver* salt is described); at the same time, carbethoxy-biuret is formed, but, being unstable in the ammonia solution, appears only as its decomposition product, cyanuric acid; biuret is formed only to a very limited extent. Ethyl allophanate is produced in 80% yield when ethylamine is used.

The course of the action of aniline on carbonyldiurethane depends largely on the temperature employed. At 110—115°, the products are diphenylbiuret, m. p. 210°, and phenylcarbethoxybiuret, NHPh·CO·NH·CO·NH·CO₂Et, m. p. 174° (the *sodium* and *silver* salts are described); the latter yields alcohol when dissolved in sodium hydroxide, and the solution on acidification gives phenyl-*iso*cyanuric acid, fine needles, m. p. 290—300° for different preparations, which forms a *silver* and a *copper* salt. (Phenylcarbethoxybiuret and phenyl*iso*cyanuric acid, together with phenylurethane and phenylallophanic ester, are produced by the action of phenylcarbimide on urethane at 130°.) At 130—150°, the products are phenylcarbethoxybiuret, diphenylbiuret in a larger yield than before, and carbonyldiphenyldicarbamide,

$$CO(NH·CO·NHPh)_2,$$

m. p. 211°. At 170°, a little phenylcarbamide, m. p. 147°, and diphenylcarbamide. m. p. 235°, are also formed, and, at higher temperatures, the latter becomes the main product.

With *o*-toluidine at 130°, phenyldiurethane yields *o-tolylcarbethoxybiuret*, fine, colourless crystals, m. p. 155—156° (from which *o-tolyliso*cyanuric *acid*, colourless needles, which do not melt below 300°, and yield a mono-*silver* salt, is obtained, as with the corresponding phenyl derivative), *di-o-tolylbiuret*, needles, m. p. 202—203°, and ethyl *o*-tolylallophanate. m. p. 137°. At 140°, the products are *o*-tolylcarbethoxybiuret, a little di-*o*-tolylcarbamide, and carbonyldi-*o*-tolyldicarbamide, m. p. 186°. At 170—180°, di-*o*-tolylbiuret, carbonyldi-*o*-tolyldicarbamide, di-*o*-tolylcarbamide, m. p. 248°, and *o*-tolylcarbamide, m. p. 188°, are obtained. Di-*o*-tolylcarbamide is the only substance isolated from experiments at 200°.

At 130—140°, β-naphthylamine yields mainly *β-naphthylcarbethoxybiuret*, colourless needles, m. p. 196° (*β-naphthyliso*cyanuric *acid* has m. p. 290—291°), with small amounts of carbonyldi-β-naphthyldicarbamide, m. p. 293°. α-Naphthylamine, on the other hand, yielded at 130° mainly *di-α-naphthylcarbamide*, m. p. 280°; smaller amounts of *α-naphthylcarbethoxybiuret*, colourless needles, m. p. 198° (*α-naphthyliso*cyanuric *acid* has m. p. 290°), and of *di-α-naphthylbiuret*, colourless crystals, m. p. 278—279°, were also produced.

The reactivity of carbonyldiurethane appears to be dependent on the presence of the carbonyl group, since neither methylenediurethane nor the substituted methylenediurethanes form metallic salts or react with amines. Thus, methylenediurethane is not attacked by aniline at 130°, traces of ammonia are evolved at 160°, and at 200° only a little diphenylcarbamide is obtained, which results from the slight dissociation of the urethane. The introduction of a phenyl group in the methylene radicle does not increase the reactivity of the substance, and, similarly, *o-nitrophenylmethylenediurethane*, colourless crystals, m. p. 190°, does not give an amide with ammonia or with aniline at temperatures up to 200°.   H. W.

Xylyloxyacetic Acids. W. GLUUD and P. K. BRENER (*Ges. Abhand. Kennt. Kohle*, 1917, **2**, 257—260; from *Chem. Zentr.*, 1919, i, 626).—Since the tolyloxyacetic acids are useful in the separation of the cresols of low temperature tars, the authors have investigated the corresponding compounds of the xylenols. p-*Xylyloxyacetic acid*, long, slender needles, m. p. 118°, is obtained in 35% yield by the action of chloroacetic acid on p-xylenol in the presence of aqueous sodium hydroxide. The *sodium* salt is described. 4-o-*Xylyloxyacetic acid*, long, colourless needles or thin, rectangular plates, m. p. 162·5°, is similarly obtained in 63% yield; the *sodium* salt is crystalline. m-*Xylyloxyacetic acid*, long, white needles, m. p. 141·6°, is prepared in 51·5% yield. *Ethyl* p-*tolyloxyacetate* is obtained from ethyl chloroacetate and sodium p-tolyloxide; it is an oil, b. p. 142—143°/11 mm., which is converted by methyl-alcoholic ammonia into p-*tolyloxyacetamide*, m. p. 128°.   H. W.

Trimethylene Disalicylate and Method of Preparing the Same. A. M. CLOVER (U.S. Pat. 1,286,944).—Trimethylene disalicylate, $CH_2(CH_2 \cdot CO_2 \cdot C_6H_4 \cdot OH)_2$, is prepared by the esterification of the glycol with twice its weight of salicylic acid in presence of half its weight of concentrated sulphuric acid at a temperature not exceeding 100°. Excess of unchanged acid is removed by washing the product with aqueous sodium carbonate at 50°, and the ester, which solidifies on cooling, is purified by crystallisation. It is a colourless, odourless substance of m. p. 77°, and has antirheumatic properties.   G. F. M.

Some Aromatic βγ-Unsaturated Ketonic Acids. R. CIUSA (*Gazzetta*, 1919, **49**, i, 164—171).—Descriptions are given of a number of unsaturated ketonic acids, obtained by the condensation of pyruvic acid with aromatic aldehydes, $R \cdot CHO + CH_3 \cdot CO \cdot CO_2H = H_2O + R \cdot CH \vdots CH \cdot CO \cdot CO_2H$.

Benzylidenepyruvic acid (compare A., 1910, i, 684) gives with phenylhydrazone a compound, m. p. 163—165° (Erlenmeyer, A., 1903, i, 698, gave m. p. 158°; 1904, i, 500), which dissolves in hot sodium carbonate solution, yields aniline when reduced with sodium amalgam, and is converted by boiling with glacial acetic acid in a reflux apparatus into a *compound*, m. p. 195° (decomp.), answering to Knorr's pyrazoline reaction; it must, therefore, be regarded as a true phenylhydrazone. The acid yields a dibromide, $CHPhBr \cdot CHBr \cdot CO \cdot CO_2H$, m. p. 124° (Erlenmeyer, *loc. cit.*, gave m. p. 138°, decomp.), decomposing at 166°. Benzylidenepyruvic acid p-nitrophenylhydrazone gives a crystalline *sodium* salt, which has been analysed.

Cinnamylidenepyruvic acid (*loc. cit.*; also Erlenmeyer, *loc. cit.*) yields a *methyl* ester, $C_{13}H_{12}O_3$, m. p. 126°, and a *tetrabromide*, $CHPhBr \cdot [CHBr]_2 \cdot CO \cdot CO_2H$, which forms white needles, turning red at 200°, m. p. 218°. The ethyl ester forms (1) a *tetrabromide*, $C_{14}H_{14}O_3Br_4$, white needles, m. p. 118°, and a *dibromide*,

$C_{14}H_{14}O_3Br_2$, yellow needles, m. p. 86°. The phenylhydrazones of the acid and of its ethyl ester exhibit the behaviour of true hydrazones.

m-Nitrobenzylidenepyruvic acid, m. p. 111° (compare Baeyer and Drewsen, A., 1883, 341), forms a *sodium* salt $(+H_2O)$ and a *dibromide*, $NO_2 \cdot C_6H_4 \cdot [CHBr]_2 \cdot CO \cdot CO_2H$, which crystallises in long, silky needles, m. p. 64°.

p-*Nitrobenzylidenepyruvic acid*, $C_{10}H_7O_5N$, forms shining, white needles, m. p. 117°. The *dibromide*, $NO_2 \cdot C_6H_4 \cdot [CHBr]_2 \cdot CO \cdot CO_2H$, crystallises in white needles, m. p. 78°.

Anisylidenepyruvic acid, $OMe \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot CO_2H$, forms yellow needles, m. p. 81°, and crystallises from alcohol with $\frac{1}{2}Et \cdot OH$. Its *sodium* salt and its *dibromide*, $C_{11}H_{10}O_4Br_2$, crystallising in white scales, m. p. 125°, were prepared.

The compound, m. p. 137–138°, described by Ryan and Dunlea (A., 1913, i, 1067) as 5-phenyl-3-styryl*iso*oxazole is probably the 3-phenyl-5-styryl*iso*oxazole obtained by the author and Terni (A., 1911, i, 918), since the action of hydroxylamine on cinnamoyl-benzoylmethane may result in the formation of two isomeric *iso*-oxazoles.   T. H. P.

The Isomeric Tropic Acids. ALEX. McKENZIE and JOHN KERFOOT WOOD (T., 1919, 115, 828–840).

Preparation of 1 : 6-Dihydroxynaphthoyl-*o*-benzoic Acid and its Salts. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 311213; from *Chem. Zentr.*, 1919, ii, 586).—1 : 6-Dihydr-oxynaphthalene is condensed with phthalic anhydride or phthalic acid in the presence of boric acid, and the acid is converted into its metallic salts by the usual methods; the presence of boric acid causes the reaction to result chiefly in the production of 1 : 6-*dihydr-oxynaphthoyl-o-benzoic acid*, whilst in the absence of a condensing agent or in the presence of substances such as zinc chloride, phthaleïns are mainly or exclusively formed. 1 : 6-Dihydroxy-naphthoyl-*o*-benzoic acid forms coarse crystals, m. p. 226—227°. The following salts are described: *monosodium* salt, pale yellow, flat prisms; the *disodium* salt is hygroscopic; *monopotassium* salt, yellow, rhombic or prismatic crystals; the *dipotassium* salt is sparingly soluble in alcohol or water; *monocalcium* salt, pale yellow, coarse crystals; *lead* salt, yellow, powdery precipitate; *copper* salt, green powder. 1 : 6-Dihydroxynaphthoyl-*o*-benzoic acid and its salts have a very sweet taste, whilst the corresponding 1 : 5-com-pound and its derivatives are tasteless. The new acid and its salts form a substitute for sugar and other sweetening agents, and also intermediate substances for the manufacture of dyes. When printed, as for chrome colours, 1 : 6-dihydroxynaphthoyl-*o*-benzoic acid gives bright greenish-yellow shades on cotton and wool which are fast to light and washing, whilst the corresponding 1 : 5-acid yields orange shades which are much less fast to light.   H. W.

The cycloPropane Series. E. P. KOHLER and T. L. DAVIS (*J. Amer. Chem. Soc.*, 1919, **41**, 992—1001. Compare A., 1917, i, 566, 570; 1918, i, 72).—One of the most characteristic properties of cyclopropane derivatives is the ease with which the ring is opened by alkyloxides, with the production of a metallic derivative of an isomeric ethylenic ester. The action has been ascribed to the addition of the alkyloxide, followed by elimination of alcohol. In the present instance, the behaviour of methyl 2-phenyl-3-methyl-3-benzoylcyclopropanedicarboxylate has been investigated, since the elimination of alcohol is here impossible owing to the presence of the methyl group in position 3; the substance, however, does not appear to be appreciably affected by sodium methoxide.

The condensation of phenyl α-methylstyryl ketone and methyl malonate is best effected by means of a solution of sodium in dry methyl alcohol at the temperature of the steam-bath; the product consists of a mixture of the two stereoisomeric forms of *methyl γ-benzoyl-β-phenylpropylmalonate,*

$$COPh \cdot CHMe \cdot CHPh \cdot CH(CO_2Me)_2$$
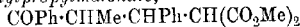
(m. p.'s 91—93° and 88—90° respectively), in addition to a considerable amount of oil. Each of the esters can be hydrolysed to the corresponding *acid* (m. p. about 160°, and thick needles, m. p. 67°, respectively), from which the *γ-benzoyl-β-phenylvaleric acids* (silky needles, m. p. 115—117°, and small, transparent needles, m. p. 92—93°) are obtained by elimination of carbon dioxide; when treated with methyl alcohol and hydrogen chloride, these two acids yield the same *methyl* ester, large, rhomb-shaped prisms, m. p. 92° (which probably has the same configuration as the dibasic ester, m. p. 92°), whilst with bromine in carbon tetrachloride solution they give *γ-bromo-γ-benzoyl-β-phenylvaleric acid,* fine needles, m. p. about 160° (decomp.), from which *γ-benzoyl-β-phenyl-γ-methylbutyrolactone,* flat, six-sided plates, m. p. 93°, is obtained by the action of sodium carbonate.

The stereoisomeric methyl γ-benzoyl-β-phenylpropylmalonates readily react with bromine, yielding the same products, namely, a small amount of *methyl γ-bromo-γ-benzoyl-β-phenylpropylmalonate,* short, coarse needles, m. p. 114—115°, and an oil; the position of the bromine atom in the solid compound is deduced from its conversion into *methyl-γ-benzoyl-β-phenyl-γ-methylbutyrolactone-carboxylate,* colourless plates, m. p. 85°, when heated, and the identity of this substance with that obtained by the half-hydrolysis of the saturated ketonic ester and the action of bromine on the ester-acid. The action of potassium acetate on methyl γ-bromo-γ-benzoyl-β-phenylpropylmalonate yields *methyl 3-benzoyl-2-phenyl-3-methylcyclopropanedicarboxylate,* $(CO_2Me)_2C<\begin{smallmatrix}CHPh\\CMeBz\end{smallmatrix}$, narrow prisms, m. p. 101°, which is not oxidised by permanganate, but is readily reduced by zinc dust and acetic acid, yielding the saturated ester, m. p. 91—93°, as sole product of the action. The ester acid, unlike the derivatives of cyclopropane previously studied, is insensitive to alkyl oxides except in the presence of moisture,

when it is hydrolysed to the corresponding *acid ester*, three-sided prisms, m. p. 162°. 3-*Benzoyl*-2-*phenyl*-3-*methyl*cyclo*propanedi-carboxylic acid*, needles, m. p. 176—178° (decomp.), is obtained by complete hydrolysis of the corresponding ester, into which it is reconverted through the silver salt; when treated with methyl alcohol and hydrogen chloride, on the other hand, the sole product is a very stable, crystalline *compound*, $C_{22}H_{26}O_7$, m. p. 158·5—159·5°.

The oily material obtained during the bromination of the methyl γ-benzoyl-β-phenylpropylmalonates was treated with potassium acetate, whereby a small further quantity of the *cyclo*propane ester already described, and an ethylenic isomeride, stout needles, m. p. 129—131°, were isolated; the latter is not reduced by zinc dust and acetic acid, and hence is not a *cyclo*propane derivative. Its most characteristic property is the readiness with which it is transformed by bases or mineral acids into an isomeric *ester*, hexagonal plates, m. p. 145°. On hydrolysis, it yields an *ester acid*, needles, m. p. about 189° (decomp.), and a dibasic acid, needles, m. p. about 180° (decomp.); these compounds, however, are probably derivatives of the ester, m. p. 145°, since this ester is obtained when the acid is esterified either by the silver salt method or by methyl alcohol and hydrogen chloride.   H. W.

Condensation of Phenyl β-Aminoethyl Ketone with Nitromalonaldehyde. WILLIAM J. HALE and EDGAR C. BRITTON (*J. Amer. Chem. Soc.*, 1919, **41**, 1020—1026).—In continuation of the work of Hale and Hoyt (A., 1916, i, 71) and of Hale and Honan (this vol., i,   ), the condensation of sodium nitromalonaldehyde with a methylene group activated by the presence of a neighbouring carbonyl group has been studied.

α-*Nitro*-β-*benzoylethylaminoacraldehyde*,
$$COPh \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH:C(NO_2) \cdot CHO,$$
small prisms, m. p. 153°, is readily produced when an aqueous solution of molar quantities of sodium nitromalonaldehyde and phenyl β-aminoethyl ketone hydrochloride is maintained at 50° for some hours. When twice the relative amount of the amino-ketone hydrochloride is used and the solution is treated with a little sodium hydroxide, β-*nitro*-α-*benzoylethylamino*-γ-*benzoylethyliminopropylene*, $COPh \cdot [CH_2]_2 \cdot NH \cdot CH:C(NO_2) \cdot CH:N \cdot [CH_2]_2 \cdot COPh$, colourless clusters of needles, m. p. 145° (*platinichloride*, m. p. 208°), is produced, which is decomposed by boiling concentrated hydrochloric acid into the nitroacraldehyde, m. p. 153°, and phenyl β-aminoethyl ketone; the compound can also be obtained by addition of sodium hydroxide to an aqueous solution of the nitroacraldehyde.   4-*Nitro*-3-*phenacylpyrrole*,
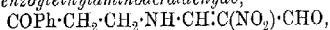
$$\begin{array}{c} C(NO_2)\!\!=\!\!=\!\!CH \\ | \qquad\qquad\quad \rangle NH, \\ CH:C(CH_2 \cdot COPh) \end{array}$$
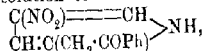
is formed by the condensation of phenyl β-aminoethyl ketone hydrochloride and sodium nitromalonaldehyde in aqueous-alcoholic solution in the presence of sodium hydroxide, or from benzoylethylaminonitroacraldehyde under similar conditions; it forms small,

lemon-yellow prisms, m. p. 170° (the *platinichloride* decomposes above 300° without melting). Attempts to oxidise the substance to a nitropyrrolecarboxylic acid were unsuccessful. The yield of the pyrrole derivative is only moderate, and the alkaline mother liquors from the preparation yield,[*] on acidification, a red, amorphous precipitate, decomposing between 127° and 132°, which appears to consist of 3-*nitro*-5-*amino*-1-*benzoylcyclopentadiene*,

$$\begin{array}{c} \text{COPh·C:CH} \\ \text{NH}_2\text{·C:CH} \end{array}\!\!> \!\!\text{CH·NO}_2.$$

H. W.

Condensation of Deoxybenzoin and Aldehydes. ANANDA KISORE DAS and BROJENDRA NATH GHOSH (T., 1919, 115, 817—820).

Condensation of Deoxybenzoin with Aromatic Aldehydes. BAWA KARTAR SINGH and JATINDRA KUMAR MAZUMDAR (T., 1919, 115, 821—825).

Action of Potassium Ferricyanide on Alizarin in Alkaline Solution. II. R. SCHOLL and A. ZINKE (*Ber.*, 1919, 52, [B], 1142—1160. Compare this vol., i, 25).—Addition of bromine to hydroxynaphthaquinonylvinylglyoxylic acid leads to the formation of β-[2-*hydroxy*-1 : 4-*naphthaquinonyl* -3-*vinylglyoxylic acid dibromide* (I), m. p. about 150° (decomp.) after softening at about 83°, which slowly loses hydrogen bromide at the ordinary temperature and forms a mixture of cumarinoid (α) (II) and *cumaroid* (β)

(I.)   (II.)
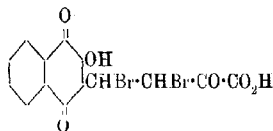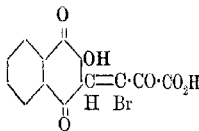
β-[2-*hydroxy*-1 : 4-*naphthaquinonyl*-3]-*a*-*bromovinylglyoxylic acids* (III), which could not be separated owing to their instability.
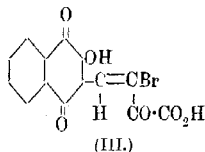
(III.)

Cumaroid Series.—*Methyl* β-[2-*hydroxy*-1 : 4-*naphthaquinonyl*-3]-*a*-*bromovinylglyoxylate*, yellow prisms, m. p. 217° (decomp.), is obtained mixed with methyl naphthafurylquinonylglyoxylate by the action of boiling methyl alcohol on the crude dibromide; the *acetyl* derivative forms pale yellow, shining leaflets, m. p. 188—189°. The *ethyl* ester has m. p. 158°. Cautious hydrolysis of the methyl ester yields the corresponding acid, m. p. 171—172° (decomp.) after previous darkening and softening, which is transformed by boiling water into naphthafuranquinone (see later), and by boiling xylene into a crystalline *acid*, m. p. about 251—252°. When heated alone at 100° or with alcohol, it is converted into bromobenzcumarinquinone. When

treated with methyl alcohol and hydrogen chloride, it re-forms the methyl ester, m. p. 216—217°. *Methyl β-naphthafuryl-3:8-quinone-1-glyoxylate* (annexed formula) crystallises in reddish-yellow needles, m. p. 222—223°, whilst the corresponding *ethyl* ester forms reddish-yellow needles, m. p. 187° (*phenylhydrazone*, brown needles, m. p. about 208—210°); the latter is oxidised by dilute nitric acid at 200° to phthalic acid. The esters are converted by methyl-alcoholic potassium hydroxide into a green salt, which is rapidly oxidised by air to a red salt, the latter being derived from naphthafuranquinonecarboxylic acid (annexed formula), the former from its dihydro-derivative. The *acid* itself forms red crystals, m. p. 298°, and yields a *sodium* salt which dissolves sparingly in water. When distilled alone or, preferably, with lime, it passes into *β-naphthafuran-3:8-quinone* (3:4-*phthalylfuran*), m. p. 210°, which is also obtained by boiling crude hydroxynaphthaquinonylbromovinylglyoxylic acid or pure β-hydroxynaphthaquinonyl-α-bromovinylglyoxylic acid with water. It yields a *monophenylhydrazone*, purple needles, m. p. 158—159°, and a *dibromide*, reddish-yellow crystals, m. p. 112—114° (decomp.), after previous softening, which slowly loses hydrogen bromide at the ordinary temperature. When boiled with glacial acetic acid, the dibromide is converted into a mixture of 1- and 2-*bromonaphthafuranquinones*, yellowish-red leaflets and red needles, m. p. 167—168°, after much softening.
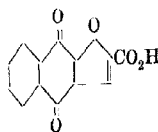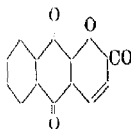
Cumarinoid Series.—4 : 5-*Benzcumarin*-3 : 6-*quinone* (3 : 4-*phthalyl-α-pyrone*) (annexed formula), brownish-yellow crystals, m. p. 214—215°, is obtained by cautiously heating silver hydroxynaphthaquinonylvinylglyoxylate in a current of carbon dioxide. 1-*Bromo*-4 : 5-*benzcumarin*-3 : 6-*quinone* is prepared by the action of boiling alcohol on crude hydroxynaphthaquinonylbromovinylglyoxylic acid; it forms yellowish-brown needles, m. p. 224—225°.

2:2-Dibromo-1:3-diketohydrindene, m. p. 175—177°, is obtained by the action of an excess of boiling bromine water on hydroxynaphthaquinonylvinylglyoxylic acid.   H. W.

The Basic Properties of Phenanthraquinone. Joseph Knox and Helen Reid Will (T., 1919, 115, 850—852).

Studies in the Camphane Series. XXXVII. Aryl Derivatives of Imino- and Amino-camphor. Martin Onslow Forster and Hans Spinner (T., 1919, 115, 889—895).

Ozonisation of *apo*Bornylene and of the different Fenchenes. Constitution of these Hydrocarbons. R. H. ROSCHIER (*Acad. Sci. Fennicae*, 1919, [*A*], **10**, 1—83; from *Chem. Zentr.*, 1919, i, 726—730. Compare Komppa and Hentikka, A., 1912, i, 278; 1914, i, 557).—*apo*Bornylene is a mixture of two isomeric hydrocarbons, one of which is the actual *apo*bornylene (I), whilst the other is tricyclic *apo*cyclene (II). Fenchene is a mixture of at least five terpenes, two of which are semicyclic, two endocyclic, and one tricyclic. Ozonisation of *d*-fenchene (Wallach's *D-l*-fenchene) has confirmed the formula (III) for it, whilst the formula IV may be ascribed with certainty to β-fenchene (Wallach's *D-d*-fenchene and Semmler's *iso*fenchene). The fenchene, b. p. 145—147°, is mainly ring-unsaturated, and probably has the constitution (V). The fenchene of lowest boiling point is identical with Semmler's *isoallo*fenchene (VI). A small amount of *cyclo*fenchene (VII) identical with Aschan's β-pinolene is contained in the fractions of fenchene of lowest boiling point.

(I.)   (II.)   (III.)

(IV.)   (V.)

(VI.)   (VII.)
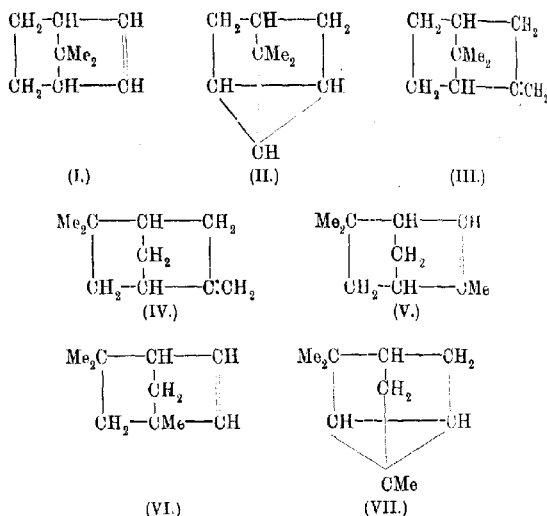
*apo*Bornylene was prepared from camphenilole by the xanthate method and from camphenilone through the dichloride; the product obtained by the first method was a completely solid, viscous, camphoraceous mass, m. p. 38°, b. p. 138°/760 mm., whilst that obtained by the second process, b. p. 138—139°, was oily at the ordinary temperature, but solidified when moderately cooled. Attempts to prepare *apo*bornylene by the distillation of

camphenilylamine phosphate in a current of carbon dioxide were unsuccessful, the original amine being recovered. Ozonisation of *apo*bornylene yielded a normal *ozonide*, $C_9H_{14}O_3$, voluminous, white powder, m. p. 55° (decomp.), which became transformed into a brown oil after some months; it decomposes quietly when heated. Fission of the ozonide by warming its solution in acetic acid yielded mainly three fractions; the most volatile was an oil, which did not reduce Fehling's solution, gave no semicarbazone, and probably consisted of apo*cyclene acetate*. The middle fraction was aldehydic, but contained some peroxide; it could not be purified by means of a crystalline semicarbazone. The apo*bornylenedialdehyde* was so unstable that it became resinified for the most part during distillation, and was converted into *apo*camphoric acid by treatment with potassium carbonate. *apo*Camphoric anhydride, m. p. 174—175°, was obtained from the least volatile fraction.

When the ozonide of *apo*bornylene obtained from camphenylone dichloride was decomposed in acetic acid solution and the latter was distilled, the distillate was found to contain apo*cyclene* (20—30% of the *apo*bornylene taken); the latter is not attacked by ozone, and is extraordinarily stable towards permanganate. It is a readily volatile, crystalline substance with a sweetish, but rather irritating, odour. It has m. p. 42·5—43°, b. p. 138—139°/764 mm., D_4^{40} 0·8710, n_D^{40} 1·45144, mol. ref. 37·80 (calc. for tricyclic, C_9H_{14}, 37·16), n_a^{40} 1·44910, n_β^{40} 1·45686, n_γ^{40} 1·46190. *apo*-Bornylene, obtained by the xanthate process, contained 62% of apo*cyclene*. Treatment with acetic acid in the presence of sulphuric acid converted apo*cyclene* into the acetate, b. p. 81—82°/8 mm., D_4^{20} 0·9971, n_D^{20} 1·4623, n_a^{20} 1·4601, n_γ^{20} 1·4729. It was hydrolysed to an alcohol, which was not obtained in a state of purity owing to lack of material, but which was identified as β-fenchocamphorol by its oxidation through β-fenchocamphorone to *apo*fenchocamphoric acid; the latter could be separated into *trans-apo*fenchocamphoric acid, m. p. 144—145°, and β-fenchocamphorone, m. p. 60—63°, characterised by its semicarbazone, m. p. 200—201°.

The α-fenchene was obtained from fenchyl chloride, and had b. p. 155—160°. $D_4^{17·5}$ 0·8670, $n_D^{17·5}$ 1·46729, a_D^{20} —32·32. The *ozonide* was a viscous, colourless oil which did not explode when heated, and contained more highly oxygenated products than the normal ozonide. After fission, it yielded about 50% of α-fenchocamphorone (identical with Wallach's *Dd*-fenchocamphorone), b. p. 198—200° (semicarbazone, m. p. 220—221°). In addition, there were formed a neutral, aldehydic. yellow oil, b. p. 120—133°, which could not be purified, and α-fenchenylanic acid (7 : 7-dimethyl-1 : 2 : 2-*bicyclo*heptane-2-carboxylic acid). m. p. 71·5—72°. The *zinc* salt is less soluble in hot than in cold water; the *anilide* forms silky needles, m. p. 149·5—150°.

The specimen of β-fenchene employed was obtained by distillation of *r*-fenchyl alcohol with potassium or sodium hydrogen sulphate in a current of carbon dioxide. It was separated into

three fractions by repeated distillation, the most volatile of which was purely endocyclic, the least volatile purely semicyclic, according to optical analysis; β-fenchene was contained in the fraction, b. p. 151—153°. β-*Fenchene ozonide* forms a viscous, syrupy oil which contains more highly oxygenated products than the normal ozonide. Fission yielded impure fenchocamphorone, which was identified by its semicarbazone, m. p. 193—195°; further oxidation of the liquid ketone led to the isolation of a little *apo*camphoric anhydride (thus proving the presence of α-fenchocamphorone as impurity), and mainly to *apo*fenchocamphoric acid (4:4-dimethyl-*cyclo*pentane-1:3-dicarboxylic acid), prisms or monoclinic plates, m. p. 144—145°; since the acid cannot be converted into an anhydride in the usual manner, it must be a *trans*-form; the zinc salt, which is less soluble in hot than in cold water, is very characteristic.

The intermediate fraction of the hydrocarbon mixture, b. p. 145—147°, behaved on ozonisation as a compound unsaturated in the ring. It is a mixture of two hydrocarbons, one of which is *isoallo*fenchene (VI), whilst the other probably has the constitution V. Fission of the ozonide yielded mainly a *dialdehyde* and a *keto-acid*. The dialdehyde, $C_{10}H_{16}O_2$, is a mobile, yellow oil, b. p. 118—120°/10 mm., D_4^{20} 1·0215, n_D^{20} 1·4700, n_* 1·4677, n_y 1·4815, which is very unstable when exposed to air, and could not be isolated in the pure state; its *disemicarbazone* crystallises in fine granules, m. p. 219°. The crude aldehyde fraction contained also a small quantity of r-*cis-iso*fenchocamphoric acid. The keto-acid, $C_{10}H_{16}O_3$, forms a viscous, yellow oil, D_4^{20} 1·0924, n_D^{20} 1·4774, which could not be caused to crystallise, and was purified by means of its *semicarbazone*, m. p. 220—221°; it contains the –COMe group, since, when treated with bromine and alkali, it yields bromoform and a dibasic acid, $C_9H_{14}O_4$, prisms, m. p. 147—148°, which, contrary to expectation, is not identical with *apo*fenchocamphoric acid obtained by the oxidation of β-fenchocamphorone. Full investigation of the acid was impossible owing to the small amount of available material, but its properties show it to be *cis-apo*fenchocamphoric acid.

Fission of the ozonide obtained from the most volatile fraction of the β-fenchene hydrocarbon mixture yielded aldehydic and acidic components, together with a small amount of a pleasant-smelling, oily *ketone*, $C_9H_{14}O$ (*semicarbazone*, m. p. 209°), which could be oxidised to an *acid*, probably $C_9H_{14}O_4$. The substances could not, however, be fully investigated owing to lack of material. The acidic fraction contained the keto-acid described above in small amount, together with r-*cis-iso*fenchocamphoric acid, m. p. 173—174°, and an aldehydic acid which, on further oxidation, was transformed into *cis-iso*fenchocamphoric acid, thus showing the fraction to consist mainly of *isoallo*fenchene (VI).

The small portion of this fraction which was not attacked by ozonisation consisted of the hydrocarbon, *cyclo*fenchene, $C_{10}H_{16}$, b. p. 142—143°, $D_4^{16\cdot5}$ 0·8624, $n_D^{16\cdot5}$ 1·45364, mol. ref. 42·73. It is

shown to be identical with Aschan's β-pinolene (VII) by its conversion into the hydrochloride, m. p. 26—28°. The *hydrobromide* has m. p. 4°, b. p. 92—93°/12 mm., D_4^{20} 1·2389, n_D^{20} 1·50570, mol. ref. 52·04. Like β-pinolene, it could be converted through the acetate into *iso*fenchyl alcohol, *iso*fenchone, and *r-iso*fenchocamphoric acid.

H. W.

Behaviour of an Alcoholic Solution of Lead Acetate towards the Resinous Substances of Colophony. I. LUDWIG PAUL (*Kolloid Zeitsch.*, 1919, **24**, 95--104, 129—138, 165—173).— The first section of this paper deals with the previously published work of Tschirch ("Die Harz und Harzbehälter," Berlin, 1906). A résumé of the results and conclusions drawn is given, and these are critically discussed. In the third section experiments on the behaviour of the resinous substances of colophony are described. A solution of powdered colophony is made in 5% sodium hydroxide, which on treatment with sodium chloride solution deposits greyish-white needles; the mother liquor, on treatment with hydrochloric acid, gives a precipitate which after washing is practically all soluble in water. On precipitating this solution with a few drops of hydrochloric acid, an acid, m. p. 123°, is precipitated. This is β-*KLw*-resin acid (colophony water soluble resin-acid). The behaviour of the various solutions of colophony with alcoholic solutions of lead acetate is also studied, and it is shown that the starting material in all previous investigations is the colloidal substance γ-pinic acid, m. p. 75—76°. This substance is slowly decomposed by the bound colloidal water in boiling alcoholic solutions. The colloidal behaviour of the components of colophony, particularly in their changes, is probably due to special holding power which resinous substances are able to exert on one another, and thereby an apparent formation of new chemical substances occurs. The residue from the *KL* substances soluble in sodium hydroxide furnishes an example of this type of substance. These extraction residues must not be confused with the decomposition products, which are obtained on washing, through the changes occurring in β-pinic acid, m. p. 98—100°, and those are probably the substances from which fossil resins are produced. Just as the resinous substances often form weak, but well-crystallised, compounds with hydrocarbons by virtue of the holding power mentioned above, so γ-pinic acid forms similar weak compounds with ethereal oils which constitute the turpentine resins. The method used by Tschirch leads to new substances which are not present in the original material. This is particularly the case for a series of amorphous substances of low melting point isolated by Tschirch from recent fossil resins. A method of separation, due to Tschirch, which leads to the acceptance of three abietic acids (α, β, and γ) is to be regarded in the above sense. Although the use of alcoholic lead acetate does not destroy the colloidal condition of the substances treated with it, for example, in the case of γ-pinic acid, yet a change in the so-called colloidal constitution is to be observed. Under the term colloidal constitution the author

understands the method of combination █████ the number of mole-
cules of colloidal water in the molecule; █████ are distinguishable by
the tannoid properties of the correspondi███ ███sin soaps and by the
decomposition and associating properties of the free resin acids.
Just as γ-pinic acid retains its colloidal water under treatment with
lead acetate, so γ-pinic acid in its weak hydrocarbon compound
retains the hydrocarbon when precipitated by the same reagent.
True resinous substances are to be distinguished from resin-like
substances. The former differ from the latter in their power of
passing into crystalline substances, the so-called absolute resins,
whereas the latter are not crystallisable. The colophony substance
is, in consequence of its colloidal nature, a living substance, which
does not come to rest until the colloidal water is used up and
thereby a labile equilibrium is set up. The stable condition is
probably reached in amber.   J. F. S.

The Mutual Influence on the Electrolytic Conductivity of Gallotannic Acid and Boric Acid in Connexion with the Composition of the Tannins.   J. BÖESEKEN and W. M. DEERNS

(*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 907—910).—The
researches of E. Fischer have shown that the tannin of the gall nut
consists principally of a mixture of the pentadigalloyl ethers of
α- and β-glucose, and if this is the case the influence of the conduc-
tivity of this substance on that of boric acid should be considerable.
Experiments have therefore been performed on the conductivity of
solutions of methyl gallate and of the tannin of the gall nut in the
presence of boric acid; the increase in conductivity is very consider-
able and markedly higher in the case of the tannin than in that of
the methyl ester, thus agreeing with the presence in the tannin of
'.en pairs of favourably situated hydroxyl groups in every molecule.
                                                          H. W.

Tannins.   II.   Chebulic Acid.   KARL FREUDENBERG (*Ber.*, 1919, **52**, [*B*], 1238—1246).

—Chebulic acid is a moderately
strong acid in which the presence of a free carboxyl group has previ-
ously been assumed, and this hypothesis is now further confirmed.
It cannot be hydrolysed by tannase, probably on account of the
inhibiting action of the acid group. When heated in aqueous
solution, the acidity increases, particularly at first, far more rapidly
than is required by the gallic acid eliminated, so that a second,
unknown acid appears to be first liberated. This is shown to be the
case, since after removal of gallic acid with ether, neutralisation of
the solution, and extraction of a crystalline tannin with ethyl
acetate, an apparently new, phenolcarboxylic acid can be isolated
in the form of its thallium *salt*; analyses of the latter have not yet
yielded absolutely concordant results, but it appears to contain
5—6% of water and to approximate in composition to thallium
gallate; it has $[\alpha]_D^{20} +34°$ ($\pm4°$) in water. The crystalline tannin,
mentioned above, has $[\alpha]_D^{18} +85°$ ($\pm4°$) in alcoholic solution, and
appears to be a digalloyl glucose. Further work on chebulic acid
is promised, but the results so far obtained seem to indicate that the

...is esterified ....two molecules of gallic acid, and that the ....d is not att.... ..o the glucose residue through its carboxyl gro.p, which is free,...t probably by a glucosidic linking. ..he use of thallium carbonate or hydroxide for the neutralisation ....tio.. after hydrolysis appears very advantageous, since it can ...y be removed by addition of halogen acid, and, in this parti-cu....instance, it also effects the precipitation of highly-coloured impurities.

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Pyrylium Compounds. IV. Hydroxypyronium Salts, their Pseudo- and Anhydro-bases. W. DILTHEY (*Ber.*, 1919, 52, [*B*], 1195—1207).—The previous work (A., 1917, i, 578, 660) has been extended to the anthocyanidines.

Phenyl styryl ketone and *p*-methoxyacetophenone react with ferric chloride in acetic anhydride solution to yield the *iron* salt, $C_{24}H_{19}O_2Cl_4Fe$, red prisms, m. p. 254—255°, which is converted by sodium carbonate into *a-hydroxy-γε-diphenyl-a-p-anisyl-Δᵃʸ-penta-dien-ε-one*, $OMe \cdot C_6H_4 \cdot C(OH){:}CH \cdot CPh{:}CH \cdot COPh$, almost colour-less, transparent prisms, m. p. 105—106° (*picrate*, slender, orange needles, m. p. 237—238°), which is slowly attacked by boiling alcoholic potassium hydr-oxide solution, yielding anisic acid. De-methylation of the enol is effected by hydro-chloric acid at 160°, whereby 2:4-*diphenyl-6-p-hydroxyphenylpyrylium chloride* (annexed formula) is formed in dark yellowish-red prisms, m. p. 293—294°. When a solution of this salt in pyridine is treated with alcohol and much water, it yields *a-hydroxy-γε-di-phenyl - a - p - hydroxyphenyl-Δᵃʸ-pentadien - ε - one*, slender, yellow needles, which darken when heated and have the same m. p. as the *anhydro-base*; the latter (annexed formula) which is best prepared by the action of heat on the enol, forms violet-blue aggregates, m. p. 164°.
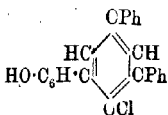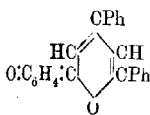
p-Hydroxyphenyl styryl ketone condenses with *p*-hydroxyacetophenone in the presence of zinc chloride and acetic anhydride to yield a complex zinc salt, from which the *platinichloride*, $C_{54}H_{42}O_{10}Cl_6Pt$, microscopic, orange needles, m. p. 258—259°, is obtained by double decomposition; the zinc salt is transformed by sodium acetate into the *diacetyl com-pound* of the *pseudo*-base,

$$OAc \cdot C_6H_4 \cdot C(OH){:}CH \cdot CPh{:}CH \cdot CO \cdot C_6H_4 \cdot OAc,$$

almost colourless, silky needles, m. p. 122° (*acid picrate*, long, yellow needles, m. p. 232—234°; *perchlorate*, orange-yellow, six-sided platelets, m. p. 249—250°). When treated with hot hydrochloric acid, the acetyl groups are removed, the *chloride* of the cyclic base being formed (annexed formula); it forms very stable, orange leaflets $(+\frac{1}{2}H_2O)$, which do not melt below 320°. It may
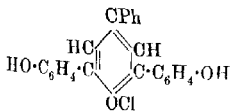
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also be prepared by demethylation of a-hydroxy-γ-phenyl-ac-di-p-anisyl-Δ^{aγ}-pentadien-ε-one with hydrochloric acid at 160°. The corresponding perchlorate ($+ \frac{1}{2}H_2O$) has m. p. 296—298°. The anhydro-base (annexed formula), slender needles, decomposing at about 340°, is conveniently prepared by addition of sodium carbonate to a solution of the perchlorate or sulphate, the chloride being too sparingly soluble for this purpose. When a solution of the base in pyridine is cautiously treated with alcohol and water, a-hydroxy-γ-phenyl-ac-di-p-hydroxyphenyl-Δ^{aγ}-pentadien-ε-one,
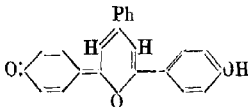
$$OH \cdot C_6H_4 \cdot C(OH) \colon CH \cdot CPh \colon CH \cdot CO \cdot C_6H_4 \cdot OH,$$
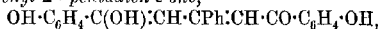
is precipitated in almost colourless, coarse needles which do not show a definite melting point; when heated at 130—140° it is re-converted into the anhydro-base.   H. W.

Cryptopine. II. WILLIAM HENRY PERKIN, jun. (T., 1919, 115, 713—790).

A New Method for a Separate Extraction of Hydrastine and Berberine from Golden Seal on a large Scale. ELSA SCHMIDT (Amer. J. Pharm., 1919, 91, 270—275).—Hydrastine is extracted from golden seal by percolation with benzene containing a trace of ammonia, and is isolated by extracting with 3% sulphuric acid and precipitating with ammonia. From the residual drug berberine is extracted by percolation with dilute aqueous acetic acid, and isolated as its hydrochloride by adding hydrochloric acid to the percolate. The author reviews the properties and uses of the two alkaloids, and the methods available for their detection and estimation.   G. F. M.

Action of Hydrogen Peroxide on Sparteine and isoSparteine. AMAND VALEUR and E. LUCE (Compt. rend., 1919, 168, 1276—1278).—Sparteine dioxide, $C_{15}H_{26}O_2N_2$, obtained by the action of hydrogen peroxide (compare Wackernagel and Wolfenstein, A., 1904, i, 917), is a strong base. Its hydriodide is not decomposed by potassium hydroxide as stated by Ahrens (compare A., 1887, 1056; 1891, 842; 1893, i, 232), but, on the other hand, the base in cold concentrated aqueous solution decomposes potassium iodide. The hydriodide, $C_{15}H_{26}O_2N_2,HI$, is reduced by hydriodic acid, giving N-hydroxysparteine periodide, $C_{15}H_{26}N_2(OH)I,I_2$, m. p. 134°, which on further reduction gives a sparteine periodide, $C_{15}H_{26}N_2,2HI,I_2$, m. p. 187°. The hydriodide of hydroxysparteine iodide, $C_{15}H_{26}N_2(OH)I,HI$, has m. p. 256—260°. Sparteine dioxide gives a methiodide, $C_{15}H_{26}ON_2(OMe)I$, m. p. 130°, which on reduction loses its methoxy-group and gives sparteine.

isoSparteine resembles sparteine in its behaviour towards hydrogen peroxide. It yields isosparteine dioxide, m. p. 115·5°, a strong

base, which decomposes potassium iodide in concentrated solutions giving an *iodide*, $C_{15}H_{26}ON_2(OH)I,2H_2O$, m. p. 83°. The corresponding *bromide* has m. p. 107—109·5°. W. G.

The Constitution of Surinamine. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, **105**, 20—24).—The author agrees with Goldschmidt (A., 1913, i, 643) that surinamine is *N*-methyltyrosine. He prepared the latter substance by the method of Friedmann and Gutmann (A., 1910, i, 741), and found that no toxic action followed the administration of 0·5 gram to a rabbit or 1 gram daily to a dog.

Surinamine (ratanhine), according to Goldschmildt, is optically active, $[\alpha]_D = -18\cdot6°$. An attempt to resolve the synthetic and inactive compound by the aid of *Penicillium* was unsuccessful. By subjecting the *N*-methyltyrosine to the action of putrefactive organisms a base was formed which was identified as *p*-hydroxyphenylethylmethylamine. J. C. D.

New Additive Compounds of Quinoline with certain Inorganic Salts. JAMES H. WALTON and CHUAN LING LIANG (*J. Amer. Chem. Soc.*, 1919, **41**, 1027—1028).—The following compounds were obtained by saturating synthetic quinoline with the requisite salt at 100°, allowing the solution to cool to the temperature of the room, and separating the crystals: *Quinoline silver thiocyanate*, $2C_9H_7N,AgSCN$, small, white crystals; *quinoline mercuric thiocyanate*, $2C_9H_7N,Hg(SCN)_2$, pale yellow crystals; *quinoline mercurous thiocyanate*, $2C_9H_7N,HgSCN$, small, colourless, shining crystals; *quinoline cupric thiocyanate*, $3C_9H_7N,2Cu(SCN)_2$, small, yellow crystals; *quinoline cuprous thiocyanate*, $2C_9H_7N,CuSCN$, yellow needles; *quinoline zinc acetate*, $C_9H_7N,Zn(C_2H_3O_2)_2$, colourless, crystalline powder; *quinoline cadmium acetate*,

$$2C_9H_7N,Cd(C_2H_3O_2)_2,$$

colourless, crystalline powder. Manganese and cobalt acetates are also readily soluble in quinoline, but do not appear to form additive compounds under the experimental conditions used. H. W.

Intermediates used in the Preparation of Photosensitising Dyes. I. Quinoline Bases. L. A. MIKESKA, J. K. STEWART, and LOUIS E. WISE (*J. Ind. Eng. Chem.*, 1919, **11**, 456—458).—The parent bases required for the production of the photosensitising dyes, pinaverdol, pinacyanol, and dicyanine are quinoline, 2-methylquinoline, and 2:6- and 2:4-dimethylquinolines. The well-known methods by which these bases may be prepared from aniline or toluidine have been investigated and certain modifications are proposed, which make it possible to work successfully with hundreds of grams of reagents at a time. The chief innovation is that extractions with ether are employed instead of steam distillations. J. C. W.

Intermediates used in the Preparation of Photosensitising Dyes. II. Quaternary Haloids. CARL H. LUND and LOUIS E. WISE (*J. Ind. Eng. Chem.*, 1919, **11**, 458—460).—The quinoline

bases mentioned in the preceding abstract are treated with an equi-molecular quantity of methyl or ethyl iodide in a round-bottomed flask connected with a reflux condenser, care being taken to modify the reaction by cooling when it has once set in, except in the case of the bases with methyl in position 2, which require prolonged heat-ing on a water-bath. The quaternary iodides obtained by the authors usually melted at the published temperatures, but higher figures are given for 2:6-dimethylquinoline methiodide, m. p. 246—247°, and 2:4-dimethylquinoline ethiodide, m. p. 223—225°.

J. C. W.

Synthesis of Photosensitising Dyes. Pinaverdol and Pinacyanol. LOUIS E. WISE, ELLIOT Q. ADAMS, J. K. STEWART, and CARL H. LUND (*J. Ind. Eng. Chem.*, 1919, **11**, 460—463).—The authors have prepared about fifteen dyes of this type by following the instructions of the original German patents (D.R.-P. 167159 of 1903 and 172118 of 1905). A product which they designate *Pv* 1 is identical with the German pinaverdol or the sensitol-green of the Ilford Co. It is made by slowly adding sodium methoxide solution to a solution of dry quinoline meth-iodide in boiling methyl alcohol, and allowing to cool slowly. It resembles splinters of brass in appearance, the crystals being mono-clinic; $a:b:c=1·1014:1:1·6053$, $\beta=88°20'$. Another product, *Pc IX*, is identical with pinacyanol or sensitol-red. It is obtained by adding a mixture of sodium hydroxide and formalin to a boiling alcoholic solution of quinoline and quinaldine ethiodides, air being first expelled, then diluting somewhat with boiling water and allowing to cool slowly. It crystallises in lustrous, bluish-green needles. There is no real evidence that quinoline ethiodide enters into the reaction at all, and if it is replaced by potassium iodide, a dye, *Pc X*, is formed, although in poor yield, which is very prob-ably identical with *Pc IX*. Like *Pv* 1, *Pc IX* is a quaternary iodide. If transformed into the chloride by reaction with silver chloride in concentrated hydrochloric acid, it gives *Pc XII*, which is more soluble than the iodide. Absorption curves are repro-duced in the original. J. C. W.

Benzidine Stannichloride. EDWARD BARNES (*Chem. News*, 1919, **119**, 13—14).—In the course of the reduction of azobenzene to benzidine by boiling with stannous chloride in hydrochloric acid, a benzidine stannichloride having the composition

$$C_{12}H_8(NH_2)_2,H_2SnCl_6$$
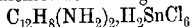
was isolated. The salt forms colourless needles, which are stable in dry air at the ordinary temperature, but evolve hydrochloric acid and stannic chloride when heated to 100°. It is considerably hydrolysed by water or dilute hydrochloric acid, and is only deposited from solution in presence of a large excess of stannic chloride. When mercuric chloride is added to a solution of the benzidine stannichloride, a mercuric salt is precipitated. The composition of the precipitate is indefinite, but by mixing hot solutions of mercuric chloride and benzidine hydrochloride in

equivalent proportions, the salt, $C_{12}H_8(NH_2),2HCl,HgCl_2$, is obtained, crystallising in transparent blades, slightly soluble in cold dilute hydrochloric acid, readily in hot.   E. H. R.

Preparation of Hydantoins. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 310427, additional to D.R.-P. 309508 and 310426; from *Chem. Zentr.*, 1919, ii, 423—424. Compare this vol., i, 351).— Substances of the types $NH_2 \cdot CO \cdot NH \cdot CRR' \cdot CO_2H$,

$$CO_2H \cdot NH \cdot CRR' \cdot CO \cdot NH_2,$$

and $NH_2 \cdot CRR' \cdot CO \cdot NH \cdot CO_2H$ (R = alkyl, R' = aryl or alkyl, with the exception of methyl or ethyl) are treated with a condensing agent, or condensation is effected without an agent by warming in the presence or absence of a solvent or diluent. The soporifics of the main patent are obtained in this manner. *CC*-Dipropylhydantonitrile, $CN \cdot CPr_2 \cdot NH \cdot CO \cdot NH_2$, colourless needles, m. p. 138°, is obtained by converting dipropyl-ketocyanohydrin by means of ammonia into the amino-nitrile, and treating the latter with potassium cyanate in hydrochloric acid solution. It is converted by boiling concentrated hydrochloric acid into *CC*-dipropylhydantoin. A solution of phenylmethyl-aminoacetonitrile in hydrochloric acid is converted by potassium cyanate into *phenylmethylhydantonitrile*, colourless needles, m. p. 217° (decomp.), which is further transformed into *phenylmethyl-hydantoin*, small needles, m. p. 197°. Ethyl *CC*-phenylmethyl-hydantoate, colourless needles, m. p. 158°, is obtained from ethyl α-amino-α-phenylpropionate hydrochloride and potassium cyanate, and yields *CC*-phenylmethylhydantoin by prolonged boiling with water or by heating alone at 200°. The same substance may also be prepared by the action of potassium hydroxide solution (33%) on *CC-phenylmethylcarbethoxylaminoacetamide*,

$$NH_2 \cdot CO \cdot CMePh \cdot NH \cdot CO_2Et,$$
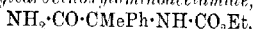
colourless needles, m. p. 191° (from α-amino-α-phenylpropionamide and methyl chloroformate in the presence of sodium carbonate). *CC*-Phenylethylhydantoin is obtained by the action of carbonyl chloride in benzene solution on phenylethylaminoacetamide; carbonyl chloride may be replaced by oxalyl chloride. CC-*Phenyl-methylthiohydantoin*, $\text{Ph} > C < \begin{smallmatrix} CO-NH \\ NH \cdot CS \end{smallmatrix}$, colourless needles, m. p. 169°, is prepared by boiling an alcoholic solution of phenylmethyl-aminoacetamide with carbon disulphide; if the thiohydantoin is dissolved in boiling sodium hydroxide solution (40%) and the solu-tion diluted with water and again boiled after addition of ferrous sulphate, *CC*-phenylmethylhydantoin is produced.   H. W.

Ethyleneguanidine and Diethyleneguanidine. P. PIERRON (*Ann. Chim.*, 1919, [ix], 11, 361—368).—Ethylenediamine in 10% solution and cyanogen bromide, when mixed in equimolecular proportions, readily react to give *ethyleneguanidine hydrobromide*, $\begin{smallmatrix} CH_2 \cdot NH \\ CH_2 \cdot NH \end{smallmatrix} > C:NH,HBr$, m. p. 125—126°. From this, by suitable

double decomposition, the *sulphate*, $(C_3H_7N_3)_2,H_2SO_4$, m. p. 281°, the *nitrate*, $C_3H_7N_3,HNO_3$, m. p. 115°, and the *hydrochloride*, m. p. 120—122°, were obtained. Attempts to isolate the base itself were not successful, but from its aqueous solution, by the action of carbon dioxide, the *carbonate*, $(C_3H_7N_3)_2,H_2CO_3$, m. p. 162°, was obtained. Ethyleneguanidine gives metallic derivatives, the *barium*, $C_3H_5N_3Ba$, *lead*, $C_3H_5N_3Pb$, *silver*, $C_3H_6N_3Ag$, and *disilver*, $C_3H_5N_3Ag_2$, derivatives being prepared.

If ethylenediamine is mixed with cyanogen bromide in the molecular proportion of 2:1, or, better still, if ethyleneguanidine hydrobromide is evaporated with an equimolecular proportion of ethylenediamine, *diethyleneguanidine dihydrobromide* (annexed formula), m. p. 224°, is obtained. From this, the *dipicrate*, $C_5H_9N_3,2C_6H_3O_7N_3$, m. p. 203°, and the *dinitrate*, $C_5H_9N_3,2HNO_3$, m. p. 138°, may be prepared.   W. C.
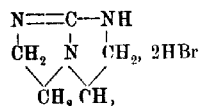
Amphoteric Colloids. V. The Influence of the Valency of Anions on the Physical Properties of Gelatin. JACQUES LOEB (*J. Gen. Physiol.*, 1919, **1**, 559—580).—The author has previously suggested a tentative theory to explain the fact that whilst gelatin salts with a univalent cation show a high degree of swelling, viscosity, osmotic pressure, and alcohol number, and gelatin salts with a bivalent metal show, for the same p_H and concentration of gelatin a low degree of swelling, viscosity, osmotic pressure, and alcohol number, yet the conductivities of the two types of salts are practically the same (this vol., i, 296). Curves representing the influence of monobasic acids (hydrochloric, hydrobromic, nitric, and acetic acids) on the osmotic pressure, swelling, and viscosity of gelatin solutions are practically identical, whereas those representing the effect of sulphuric acid are much lower, and stand very much in the same relation to the curves of the monobasic acids as do the curves for calcium gelatinate to those for sodium gelatinate.

The curves representing the influence of other dibasic acids, namely, oxalic, tartaric, succinic, citric, and phosphoric acids, are practically identical with those of the monobasic acids. If the author's theory is correct and it is true that the effect of an electrolyte on the physical properties of the colloid is due to the formation of real chemical compounds between the colloid and one of the ions of the electrolyte, it should be possible to prove, first, that twice as many molecules of hydrobromic acid as of sulphuric acid combine with a given mass of gelatin, and secondly, that the same number of molecules of phosphoric, citric, tartaric, oxalic, or succinic acid combine with the same mass of gelatin as of nitric or hydrochloric acid. The present paper gives experimental proof that both these conditions hold.

Gelatin sulphate and gelatin bromide solutions possessing the same p_H have practically the same conductivity. Hence the difference in effect of sulphates and bromides on the physical properties

of gelatin cannot be due to the different ionising and hydration effects of the two acids on the protein molecule.   J. C. D.

Pekelharing's Pepsin. V. The Inhibition of the Action of Pepsin by the Bile Acids. W. E. RINGER (*Arch. Néerland. Physiol.*, 1919, **3**, 349—360).—The bile acids inhibit the proteolytic action of pepsin. This is not due to a destruction of the enzyme, for if the bile acids are removed by dialysis the proteolytic activity of the pepsin is restored to its original value. The inactivation is probably a result of adsorption phenomena, and the action of the bile acids closely resembles that of certain ions such as the ferrocyanide ion.   J. C. D.

Physiological Chemistry.

The Presence of Phosphates in Human Blood-serum. VIII. The Partition of Phosphorus, with Especial Reference to the Phosphorus in Combination with Proteins. JOH. FEIGL (*Biochem. Zeitsch.*, 1919, **94**, 293– 303. Compare A., 1918, i, 50, 203, 320, 357; this vol., i, 138).—A further study of the distribution of phosphorus in human blood in normal and pathological cases.   J. C. D.

The Presence of Phosphate in Human Blood-serum. IX. A Study of Methods and the Distribution of Phosphorus in Normal Erythrocytes. JOH. FEIGL (*Biochem. Zeitsch.*, 1919, **94**, 304—312).—The methods and technique are discussed, and figures representing the distribution of phosphorus in the normal red blood cells are given.   J. C. D.

Physical Scheme for the Study of the Mineral Nutrition of the Cell. PIERRE GIRARD (*Compt. rend.*, 1919, **168**, 1335—1338). Working on the lines of his previous experiments (compare A., 1908, ii, 456; 1909, ii, 463), the author shows that, in the case of a solution of barium chloride, the barium and chlorine ions will diffuse through a membrane into water, at different proportional rates, according as the solution is acidified with a trace of nitric acid or made alkaline with a trace of ammonia, polarisation occurring at the membrane. These experiments are quoted in further support of his views on the selective permeability of living membranes (*loc. cit.*).   W. G.

Enzyme Studies on Cellulose Degradation Products. HANS PRINGSHEIM and ADELHEID MAGNUS VON MARKATZ (*Zeitsch. physiol. Chem.*, 1919, **105**, 173—178).—The authors have prepared a cellulose dextrin free from products yielding an osazone reaction

by the method of Madsen (Inaug. Diss., 1917). No evidence of this substance being degraded by the action of diastase could be obtained, nor did emulsin, by virtue of its cellobiase, bring about the formation of any products yielding osazones. Extracts of the first stomach, small intestine, and pancreas of oxen, likewise, had no hydrolytic action, so the conclusion is reached that in the intestinal tract of these animals cellobiose is split by the action of bacteria. Cellobiose is not oxidised to cellobionic acid on boiling with yellow mercuric oxide. J. C. D.

The Stability of Lactalbumin towards Heat. A. D. EMMETT and G. O. LUROS (*J. Biol. Chem.*, 1919, **38**, 257—265).— The biological value of lactalbumin as a protein for growth did not appear to be diminished by heating at 90—100° in an air oven for sixteen hours, or by treatment in an autoclave at fifteen pounds pressure for two or six hours. There was certainly no evidence that the heated protein was toxic for young rats. The previous conclusions regarding the excellent growth-promoting value of lactalbumin (this vol., i, 363) is further substantiated on the hypothesis that there is a vitamine factor involved which is different from the so-called water-soluble *B*. J. C. D.

The Nutritive Value of Yeast Protein. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1919, **38**, 223—227).— Rats were kept for more than a year, covering the period of growth, on a diet in which yeast furnished the sole source of nitrogen, as well as of the water-soluble vitamine. The animals showed a normal rate of growth, but certain cases exhibited sterility on arriving at maturity. This is not attributed to the presence of a toxic factor in the yeast. J. C. D.

The Zinc Content of some Food Products. VICTOR BIRCKNER (*J. Biol. Chem.*, 1919, **38**, 191—203).—The author found the method proposed by Breyer (Scott, "Standard Methods of Chemical Analysis," 1917, 487) satisfactory for the estimation of very small quantities of zinc. Hen's eggs contain about 1 mg. of zinc, of which practically all is present in the yolk. Ordinary market milk contains on an average 4·2 mg. of zinc per kilo, but variations are to be found in the milk from different animals. The zinc content of human milk is markedly higher than that of cow's milk. The presence of zinc both in egg yolk and in milk suggests that this element may exert an important function in nutrition. J. C. D.

The Degradation of Fatty Substances in the Central Nervous System. ELSE HIRSCHBERG and HANS WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, **105**, 1—19).—The amount of alkali bound after boiling the spinal cord of the frog with $N/10$-sodium hydroxide for two hours may be taken as a measure of the amount of fatty substances present. Using this method of estimation, the authors have shown that the fat content of the surviving cord

gradually diminishes when it is kept in an atmosphere of oxygen or in oxygenated physiological saline solution. The decrease is due to oxidation processes, and is more marked when stimulation is applied. Considerable fat-sparing action may be shown by certain carbohydrates; thus, dextrose may reduce the utilisation of fatty substances some 40% in resting metabolism, and as much as 80% in stimulation. Reasons are given for believing that the substances which bind alkali on hydrolysis, and are utilised during oxidation, are of the nature of phosphatides rather than of true fats.   J. C. D.

The Protein Sugar. HENRI BIERRY *(Compt. rend.*, 1918, **168**, 1225—1228. Compare Bierry and Fandard, A., 1914, i, 218, 454, and Bierry and Ranc, A., 1914, i, 346).—If the muscle plays a part in the genesis of protein sugar, differences in the protein sugar content should be found between the arterial plasma and venous plasma from the same group of muscles. This has been shown to be true for the group of muscles of the thigh in the case of the dog. The author suggests that in the muscular protoplasm there exists a complex nitrogenous molecule, the nucleus of which remains invariable, but has attached to its terminal chains peptidic groupings capable of being liberated and then regenerated. These groupings can unite with dextrose and block its aldehyde function.
                                                                                                                                  W. G.

Colours of Colloids. VI. Blue Eyes. WILDER D. BANCROFT *(J. Physical Chem.*, 1919, **23**, 356—361. Compare this vol., ii, 275, 324).—In the present paper the colour of blue eyes is discussed. It is shown that there is no pigment on the front of the iris in blue eyes, the blue colour is due to turbid media and is richer the finer the suspended particles. When the uvea is lacking, the colour of the blood shows through and albinism is the result. All other colours in eyes are due to pigmentation on the front of the eye, which either modifies or masks the blue of the turbid media.
                                                                                                                                  J. F. S.

Zinc in Oysters. R. S. HILTNER and H. J. WICHMANN *(J. Biol. Chem.*, 1919, **38**, 205—221).—Zinc was invariably found present in the oysters, all of which were grown in Atlantic waters. It is probable that copper is always associated with the zinc. The amount of zinc found could not be correlated with the weight of the system or with the zinc content of the water in which they grew. Considerable quantities of zinc and sometimes traces of copper were detected in the vegetation and organic matter dredged up with the oysters.

It appears probable that zinc and copper can be absorbed by the tissues of the oysters in quantities far in excess of functional requirements.   J. C. D.

Pyrrole and Melanuria. PIETRO SACCARDI *(Atti R. Accad. Lincei*, 1919, [v], **28**, i, 309—311).—Subcutaneous administration

of pyrrole to a rabbit produces a green coloration of the urine, which afterwards becomes brown. Such urine exhibits no patho-logical characters, retains its normal alkalinity, and responds to the reactions regarded as characteristic of the melanogens.   T. H. P.

Hæmatoporphyria Congenita. II. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1919, **105**, 158—172).—The daily excretion of crude porphyrin in the urine in cases of this disease was found to be fairly constant at various periods during two years. Analyses of crude porphyrin from urine gave higher values for carbon and lower values for hydrogen and nitrogen than were recorded by Fischer (A., 1916, i, 514). The figures for nitrogen are markedly higher than the nitrogen content of free urinoporphyrin, so that it is prob-able that the crude product is a chemical or physical complex of the pigment with a substance rich in nitrogen. Analyses of purified porphyrin-methyl ester from urine agree with the formula deduced by Fischer, $C_{47}H_{50}O_{16}N_4$. Analyses of the porphyrin methyl ester from fæces agree with Fischer's formula, $C_{39}H_{42}O_8N_4$. The author confirms his previous observation of the occurrence of porphyrin and hæmatin in the blood of patients with this disease, and now finds considerable amounts of bilirubin also.   J. C. D.

New Theory relating Constitution to Taste. Simple Relations between the Constitution of Aliphatic Compounds and their Sweet Taste. ERNEST OERTLY and ROLLIN G. MYERS (*J. Amer. Chem. Soc.*, 1919, **41**, 855—867).—A preliminary paper, in which a theory of the cause of the taste of sweet substances is put forward. The taste of sweet substances depends on two factors, the presence of a glucophore and an auxogluc. An auxogluc is an atom or radicle which, combined with any glucophore, yields a sweet compound. A glucophore is a group of atoms which has the power to form sweet compounds by uniting with a number of otherwise tasteless atoms or radicles. This theory is considered in the present paper only in connexion with aliphatic compounds. In the sense of the theory the following radicles are glucophores:

(1) $-CO\cdot CH(OH)-(+H)$;

(2) $CO_2H\cdot CH(NH_2)-$; (3) $-CH_2\cdot O\cdot NO_2$; (4) $CH_2(OH)\cdot CH(OH)-$;

(5) $C^{H_2-x}_{Hal\,x}$; (6) $C^{H_2-x}_{Hal\,x}\cdot C^{H_2-y}_{Hal\,y}$. The following atoms or radicles act as auxoglucs, forming sweetish compounds with glucophores: (*a*) hydrogen, (*b*) the radicles C_nH_{2n+1}, containing 1—3 carbon atoms, (*c*) the radicles $C_nH_{m+1}\cdot O-$, of the monohydric alcohols, where $n=1$ or 2, (*d*) the radicles $C_nH_{2n-1}O_n$ of the polyhydric alcohols. A very long list of sweet substances supporting this theory is given. The presence of the phenyl group tends to make an otherwise sweet compound bitter. Thus ethylene glycol is sweet, but its phenyl derivative is slightly bitter. Some exceptions to the rule are found in stereoisomeric substances; thus *l*-valine, $CHMe_2\cdot CH(NH_2)\cdot CO_2H$, is made up of the glucophore,

$$-CH(NH_2)\cdot CO_2H,$$

and the auxogluc, CHMe₂–, and is slightly bitter, but *d*-valine and *dl*-valine are both sweet. J. F. S.

Is there a Relationship between the Power of Absorbing Radiant Heat and the Odour of Substances? G. GRIJNS

(*Arch. Néerl. Physiol.*, 1919, **3**, 377—390).—The various attempts which have been made to trace a relationship between the odour of substances and their chemical constitution or physical properties are reviewed. Tyndall ("Heat as a Mode of Motion," London, 1865, 366) observed that gases with an odour possessed the power of absorbing radiant heat to a marked degree. The author has attempted to study this point more fully and quantitatively. An apparatus, termed an odorimeter, devised by Prof. Zwaardemaker for the quantitative measurement of odours is described. No relation between the intensity of the odour and the power of absorbing radiant heat is detected, and it is therefore concluded that the stimulation of the olfactory apparatus is not effected by the liberation of energy absorbed from radiant heat. J. C. D.

The Biological Action of Thorium. H. JASTROWITZ

(*Biochem. Zeitsch.*, 1919, **94**, 313—358).—No demonstrable influence of thorium on nuclease or uricolysis was observed. After injections of thorium into dogs, there was a tendency for a higher excretion of uric acid than normally. The fact that thorium may delay the separation of uric acid from its supersaturated solution in serum is held to be of importance from a clinical point of view. The peptolytic enzymes are not influenced by thorium, but the peroxydase is inhibited. J. C. D.

Genesis of Thiocyanic Acid in Animals. VI. SERAFINO

DEZANI (*Arch. Farm. sperim. sci. aff.*, 1918, **26**, 115—128; from *Chèm. Zentr.*, 1919, i, 485—486. Compare this vol., i, 138).—It has been shown by Bruylants that carbon disulphide is converted into thiocyanic acid by the animal organism. Thiocarbamide appears to be a possible intermediate compound, since its presence in the organism has been detected by Gautrelet. In the case of the rabbit, administration of thiocarbamide did not lead to an increase in the thiocyanic acid in the urine. In the cases of both the rabbit and the dog, elimination of the acid depends greatly on the nature of the nourishment. It is very small when clover is given, but very marked with cauliflower. Its origin with the rabbit is exogenic in nature. H. W.

Effect of Various Aromatic Substances on the Blood Vessels. Comparison of the Constitution and Action of Drugs. S. KONDO (*Kyoto Igaku Zasshi*, 1917, **14**, No. 7, 25—75; *Jap. Med. Literature*, 1919, **4**, 18).—The compounds studied were vasodilators, similar in action but differing in degree. They stimulated first the nerve, then the muscle fibre, and vascular paralysis was produced. With few exceptions, if the vasodilator was given

sufficient time to act, the vasoconstrictor action of barium and of adrenaline was prevented. The physiological action of compounds of the aromatic series is due to the benzene nucleus, and is modified by substituents. Monohydric phenols had a more powerful action than either benzene or dihydric or trihydric phenols; a similar relation existed between sodium benzoate and salicylate, and between *cyclo*hexanol and quinitol (*cyclo*hexane-1:4-diol). Of the three isomeric dihydroxybenzenes, resorcinol exerted the greatest vasodilator action. Guaiacol was more powerful than catechol, phenacetin than antifebrin, lactophenine than aniline, phenyl-hydrazine than aniline. The toxicity was increased by the union of two nuclei. Naphthalene was more toxic than benzene, benz-idine than aniline, and quinoline than pyridine. Menthol and camphor had an identical action; pyridine and nicotine acted similarly, likewise quinoline and quinine. *cyclo*Hexane was more powerful than benzene, and piperidine than pyridine. *cyclo*-Hexanol did not exert a more marked action than phenol.

CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture.

Biochemical Action of Microbes on Sugars and Alcohols. A. BESSON, A. RANQUE, and CH. SENEZ (*Compt. rend. soc. biol.*, 1918, **81**, 930—933; from *Chem. Zentr.*, 1919, i, 663–664).—A table is given showing the action of various microbes (*Bacillus faecalis alkaligenes*, *B. pyocyaneus*, *B. Shiga*, *B. Hiss*, *B. Flexner*, *B. typhi*, *Vibrio cholerae*, *B. proteus*, *B. paratyphi A*, *B. para-typhi B.*, *B. coli*) on dextrose, lævulose, maltose, dulcitol, sucrose, lactose, mannitol, and glycerol in the presence of agar or peptone water. The mode of action depends greatly on the form of nutri-ment, and the manner in which the different sugars and alcohols are attacked does not depend on the nature of the substances, but is a specific property of the respective microbes. The evolution of gas seems to be a more important phenomenon than the fact that a particular sugar is or is not attacked. With regard to their action on sugars and alcohols, microbes may be conveniently classified as follows: (i) inactive microbes which do not attack these substances; (ii) microbes which act without evolving gas; (iii) such as act with evolution of gas. The latter two groups may be sub-divided according to the susceptible individual compounds.

H. W.

Benzoic Acid as a Disinfectant. H. P. KAUFMANN (*Zeitsch. angew. Chem.*, 1919, **32**, 199—200).—The bactericidal action of benzoic acid on bouillon cultures of *Staphylococcus* and diphtheria bacilli was investigated, and concentrations as low as 0·08% in the former case and 0·04% in the latter were found to produce

sterility in five days. In steam or water vapour at temperatures as low as 37°, benzoic acid showed a powerful bactericidal action comparable with that of phenol under similar conditions. The volatility of benzoic acid in water vapour from boiling aqueous solutions was determined by passing the vapours through a condenser and estimating the benzoic acid in the distillate. With 1% solutions, the percentage gradually increased from 0·256 at the commencement to 1·088 when 90% of the solution had been distilled off, at which point the remaining acid began to separate as an oil. With 2·5% solutions, the benzoic acid content of the distillate rose from 0·605% initially to 1·006% when 70% had distilled and oil began to separate. With 5% solutions, the corresponding figures were 0·995%, rising to 1·06% when 30% had distilled over. [See, further, *J. Soc. Chem. Ind.*, 1919, August.]   G. F. M.

Increase of the Action of Catalase in Yeast Cells.

HANS VON EULER and RAGNAR BLIX (*Zeitsch. physiol. Chem.*, 1919, **105**, 83—114).—The researches of Phragmén (*Medd. K. Vetenskaps-akad. Nobel-Inst.*, 1919, 5) have shown that fresh yeast can bring about the decomposition of dilute hydrogen peroxide. The decomposition follows, within certain limits, the course of a unimolecular reaction. The reaction constant increases proportionately to the amount of yeast used. The power of decomposing hydrogen peroxide possessed by the living yeast may be increased from two to six times by the addition of small quantities of protoplasmic poisons, such as chloroform, thymol, toluene, and phenol. Analogous cases have been described (Euler and Johansson, A., 1912, i, 807). The catalase action of yeast is also greatly increased by drying at the ordinary temperature, or by dehydration by other means—treatment with alcohol or acetone—provided the enzyme is not destroyed. No appreciable increase in the catalase action of the dried yeast was observed to follow the addition of chloroform or toluene. When emulsions of fresh yeast are maintained at 55—63° for from one-half to two hours, there is also a very great increase in the power of decomposing hydrogen peroxide. Such activation is not confined to yeast, but is also found in the case of numerous other organisms.

The catalase action per cell may be raised by treating the yeast with nutritive solutions containing sucrose. The influence of a reducing agent, such as methylene-blue, is to cause an increased activation of catalase, whereas acetaldehyde has an inhibitory action.

The influence of dehydration and of protoplasmic poisons on the enzymes of yeast is discussed, and it is considered not improbable that in the case of catalase they act by preventing or neutralising the action of an inhibitory factor.   J. C. D.

Antagonism between Alkaloids and Salts in Relation to Permeability.

W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, **1**, 515—519).—It was found that nicotine, caffeine, and cevadine may

antagonise the action of sodium chloride. They decrease permeability, and resemble in this respect salts, such as calcium chloride, which antagonise sodium chloride. J. C. D.

Two Crystalline Salts from the Phospho-organic Reserve Principle of Green Plants. S. POSTERNAK (*Compt. rend.*, 1919, **168**, 1216—1219. Compare A., 1903, ii, 607, 679, 680).—The author describes methods for preparing two crystalline phospho-organic salts from seeds or from phytin. The first salt is a double sodium calcium salt having the composition $C_6H_{12}O_{27}P_6Ca_2Na_8$, and crystallising in slender needles. The second is a *sodium* salt, $(C_2H_4O_9P_2Na_4)_3,44H_2O$. It crystallises in prisms, and readily yields the corresponding *copper* and *lead* salts. W. G.

The Constitution of the Phospho-organic Reserve Principle of Green Plants. S. POSTERNAK (*Compt. rend.*, 1919, **169**, 37—39. Compare preceding abstract).—The author now inclines to the view that this material is an inositol hexaphosphate which energetically retains 3 mols. of water, and these cannot be removed without decomposing the compound. W. G.

Studies on Enzyme Action. XVII. The Oxydase, Peroxydase, Catalase, and Amylase of Fresh and Dehydrated Vegetables. K. GEORGE FALK, GRACE MCGUIRE, and EUGENIA BLOUNT (*J. Biol. Chem.*, 1919, **38**, 229—244).—The oxydase reactions with carrot, yellow or white turnip, potato, and tomato juices are greatly increased on dilution. Apparently some substance, chemically unsaturated, is present which combines with the oxygen, preventing it from acting on the reagent. The peroxydase reaction did not show such increase on dilution. There is no well-defined hydrogen-ion concentration for the maximum action with oxydase, peroxydase, or catalase, but the reactions are, in general, better between p_H7 and $p_H'10$. They are inhibited by acid reaction, except in the case of the tomato. Vacuum dehydrated cabbage and carrot gave more marked oxydase reactions than did the fresh vegetables, but in every other case the enzyme action was less after dehydration. Well-defined maxima in the amylase reactions are apparent in cabbage, carrot, and turnip juices at about p_H6. Dehydration causes a decrease in the activity of this enzyme. J. C. D.

A Component of the Fat of Bassia longifolia L. (Illipe Malabrorum Kön) and Bassia latifolia. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, **105**, 31—32).—On preserving pieces of the press cake of seeds of *Bassia longifolia* and *B. latifolia* in an evacuated vessel over phosphoric oxide for several months at 30—35°, the surface of the cake became covered with fine, needle-shaped crystals. These were identified as palmitic acid. J. C. D.

The Resin of the Outer Bark of Melaleuca uncinata. HENRY G. SMITH (*J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 232—237).—The thin, paper-like epidermis of the stems and

branches of *Melaleuca uncinata* contains from 20—25% of a resin, which can be extracted with hot alcohol. The resin resembles ordinary shellac in appearance and has D^{15} 1·135. About 70% of the total resin is an acid resin, m. p. 148—150°, which gives a *potassium* and a *silver* salt. The neutral substances constitute about 25% of the original resin.

In addition to the resin, the outer bark contains a small amount of a vegetable wax, m. p. 67—68°. W. G.

Isolation of a Saponin from Platycodon grandiflorum Root. H. OSHIKA (*Kyoto Igaku Zasshi*, 1918, 15, No. 2, 76—83 ; *Jap. Med. Literature*, 1919, 4, 20).

—The root of the herbaceous plant *Platycodon grandiflorum* (Japanese " Kikyo," Chinese " Kihkang " or " Kihung ") is used as an astringent, carminative, sedative, and vermifuge. It contains a *saponin*, which has the formula $C_{35}H_{48}O_{20}$, is a white powder when pure, is sparingly soluble in water, more readily so in alkali, and is insoluble in acids, ether, and chloroform. Its hæmolytic power is approximately one half that of dioscin. The infusion or decoction of the root has a toxicity for the mouse approximately equal to that of senega root.

CHEMICAL ABSTRACTS.

Composition of Inclusion Cells and their Relation to the Mellowing of Fruits. C. GRIEBEL and A. SCHÄFER (*Zeitsch. Nahr. Genussm.*, 1919, 37, 97—111).

—The mesocarp of certain fruits (especially the *Pyrus* species) consists solely of cells containing tannins, and the term "inclusion" cells is given to them, as a distinction from the tannin idioblasts of other fruits and plants. When ripe, fruits having such a mesocarp rapidly become over-ripe or mellow. The single exception, as regards mellowing, is the fruit of *Prunus spinosa* (sloe). The disappearance of the astringent taste during mellowing is not due to decomposition of the tannins, but to their becoming insoluble. The inclusion cells of *Pyrus domestica* contain a tannin which is soluble in water and alcohol; this tannin is, in part, combined with a sparingly soluble colloidal substance of unknown composition; only when the fruit mellows or is dried do the cell contents become insoluble, brown-coloured substances being formed gradually as this change takes place. Acetaldehyde is formed during the mellowing. The quantity of pentosan and galactan in the inclusion cells of *P. domestica* is very small, and sugars do not appear to be present. The unchanged tannin in the cells yields the reactions of *o*-hydroxy-compounds, an indication that it is a catechol derivative; fusion with potassium hydroxide yields a small quantity of protocatechuic acid, but no phloroglucinol. The tannin possesses no glucosidal character, and its properties resemble those of the oak-bark tannins. W. P. S.

The Presence of Aconitic Acid in Sugar-cane Juice and a New Reaction for the Detection of the Acid. CHARLES SOMERS TAYLOR (T., 1919, 115, 886—889).

Effect of Manganese Compounds on Soils and Plants.
E. P. DEATRICK (*Cornell Univ. Agric. Exp. Sta. Mem.*, 1919, 19, 371—402).—Manganese salts at high concentrations decrease the growth of wheat in water cultures; at lower concentrations, they stimulate the growth of the plants and increase the oxidising power of the roots. The presence of nutrient salts and the food stored in the endosperm of the wheat seed reduce the toxic effect of the manganese salts. The toxic effect is shown by a browning of the roots and a bleaching of the leaves. The bleached leaves of plants treated with manganese salts contain more manganese than the green leaves. Manganese salts added to the soil increase the power of the soil to oxidise aloin and phenolphthalein. This the author believes is due to the formation of manganese dioxide. Low concentrations of manganese salts stimulate the ammonification of dried blood, but inhibit the nitrification of ammonium sulphate in the soil.   CHEMICAL ABSTRACTS.

Acidimetric Titration of Grain Extracts and Amino-acids in the Presence of Alcohol. VICTOR BIRCKNER (*J. Biol. Chem.*, 1919, 38, 245—254).—It was found that a larger amount of alkali is required to neutralise the acidity of grain extracts when alcohol is present. A study of this point showed that amino-acids, which in aqueous solution are nearly neutral to phenolphthalein, react distinctly acid in the presence of alcohol. The suggestion is advanced that this may be due to an interaction between the hydrated form of the amino-acid and the alcohol.   J. C. D.

Constituents of Emmenthaler Cheese. V. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, 105, 25—30. Compare A., 1902, ii, 687; 1904, ii, 585; 1906, ii, 248; 1909, ii, 423).—It has been previously shown that the usual protein cleavage products can be isolated from this cheese, with the one exception of arginine. Arginine was not present in several kinds of skimmed-milk cheese examined. The fate of the arginine has been inquired into. This amino-acid might by ferment action give rise to agmatine, 1:4-diaminobutane, ornithine, urea, and ammonia. 1:4-Diamino-butane was not present, but the presence of urea and ornithine was established. Traces of *p*-hydroxyphenylethylamine were also detected.   J. C. D.

The Statement of Acidity and Alkalinity, with Special Reference to Soils. EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1919, 9, 305—309).—The author proposes a new method of expressing acidity or alkalinity in place of the usual potential method, in which the value $P_H = 7$ indicates neutrality. His scale for chemical potentials is such that $X_H = 0$ indicates neutrality, acidity being expressed by positive values and alkalinity by negative. These new values may be arrived at by subtracting the values of P_H from 7.   W. G.

General and Physical Chemistry.

Optical Properties of Magnesium Platinocyanide. P.
Aubert (*Bull. Soc. franç. Min.*, 1917, **40**, 177—182; from *Chem.
Zentr.*, 1919, i, 509).—The author has redetermined the optical
constants of magnesium platinocyanide, $MgPtCy_4,7H_2O$, since the
data recorded in the literature are discordant. The following
indices of refraction are found for the usual lines: $B(687)=1.5546$,
$C(653)=1.5585$, $D(589)=1.5608$, $E(527)=1.57$.   H. W.

**The Modifications Produced in the Spark Spectra of
Different Metals by the Surrounding Medium.** Bouchetal
de la Roche (*Bull. Soc. chim.*, 1919, [iv], **25**, 305—309).—Spark
spectra between metallic electrodes in oxygen or oxidising gases,
such as carbon dioxide or nitrous oxide, are similar to those
obtained in air and undergo the same change when a self-induction
coil is introduced into the circuit. The spectra in reducing gases,
such as hydrogen, illuminating gas, etc., are different, being very
poor in rays, and if the self-induction coil is introduced, the metallic
spectrum is still further enfeebled. This phenomenon varies in
intensity with the metals examined, and the author gives the
principal rays which persist in a number of metallic spectra in
hydrogen or hydrocarbons.   W. G.

Series Spectrum of Helium. A. Landé (*Physikal. Zeitsch.*,
1919, **20**, 228—234).—A mathematical paper in which relation-
ships between the structure of the helium spectrum and the series
spectra are discussed.   J. F. S.

Regularities in the Spectra of Lead and Tin. R. V.
Zumstein (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 59—63).
—An examination of the lead spectrum shows that there are five
series of three lines, the corresponding members of which have
constant frequency difference, the heads of these series being the
lines 7229.30, 4057.97, 3683.60, 3639.71, and 2833.17. Similarly,
tin shows five groups of three lines each with constant frequency
difference, the heads of each group being the lines 3801.16, 3175.12,
3009.24, 2863.41, and 2840.06.   W. G.

New Lines in the Extreme Ultra-violet of certain Metals.
D. S. Ainslie and D. S. Fuller (*Trans. Roy. Soc. Canada*, 1918,
[iii], **12**, III, 65—78).—The vacuum arc spectra of lead, tin, iron,
nickel, cobalt, thallium, copper, aluminium, zinc, and carbon have
been studied from λ 2400 to λ 1400. The vacuum arc spectra
obtained for copper, zinc, and aluminium were found to correspond
with the results obtained for the spark spectra. The results
obtained for tin, lead, and thallium between λ 2400 and λ 1800

agree fairly well with those obtained by Saunders (compare *Astr. Phys. J.*, 1913, **43**, 234). Several new lines between λ 1800 and λ 1400 were observed and measured.

W. G.

Arc Spectrum of Scandium. SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 438—439).—The arc spectrum of scandium from wiikite has been photographed and the lines measured. The arc was produced between poles made by compressing a mixture of silver powder and scandium oxide. On the same plate, photographs were obtained of (i) iron, (ii) scandium and silver, and (iii) silver. In this way the silver lines were eliminated and the wave-length of the scandium lines deduced from the iron lines. A table is given containing 101 lines between λ 2420·025 and λ 6305·7. A photograph of the spectrum is reproduced in the paper.

J. F. S.

The Constitution of the Atom and the Properties of Band Spectra. H. DESLANDRES (*Compt. rend.*, 1919, **168**, 1179—1185). —Based on the formula

$$\nu = \pm f(n^2 p^2)(m + a)^2/2 + B(n + \beta)^2/2 - C(p + \gamma)^2/2 \pm K$$

(compare this vol., ii, 206), the author indicates a new method for classifying band spectra.

W. G.

The Absorption Spectra of the Nitric Esters of Glycerol. HARRY HEPWORTH (T., 1919, **115**, 840—847).

Researches on Pasteur's Principle. F. M. JAEGER (*Rec. trav. chim.*, 1919, **38**, 171—316).—This paper contains a full, detailed account of the author's crystallographic and optical researches on those complex metallic salts which can be separated into *d*- and *l*-optically active isomerides (compare A., 1915, i, 867; ii, 399; 1918, i, 3, 7; this vol., i, 5, 8, 252). The salts described fall into three groups: (1) complex salts of tervalent chromium, cobalt, and rhodium with three molecules of ethylenediamine; (2) complex salts of iron, chromium, cobalt, rhodium, and iridium with three radicles of oxalic acid; (3) analogous salts of iron, chromium, and rhodium with three radicles of malonic acid. The existence of geometrical enantiomorphism in these salts is explained by Werner's octahedral distribution of the three similar bivalent radicles about the central metallic atom, and it is pointed out that, although the optically active molecules are dissymmetrical, they are not asymmetrical, but contain certain elements of symmetry, among others a three-fold axis, which sometimes also appears in the actual crystals. The optical rotatory power of these salts is often extremely high. There appears to be no direct connexion between the optical rotation and the appearance of enantiomorphous hemihedral forms on the crystals. These forms usually appear in the derivatives of oxalic and malonic acids, but rarely in those of ethylenediamine. It is concluded that the magnitude and the intensity of the rotatory power of the dissymmetrical molecules

are not dependent on chemical contrast among the substituents distributed around the central metallic atom, but that the appearance of enantiomorphous hemihedral forms is favoured by such contrast. E. H. R.

The **Phenomena of Luminescence** accompanying the **Oxidation of Potassium or Sodium.** G. REBOUL (*Compt. rend.*, 1919, **168**, 1195—1196).—The author finds that the presence of moisture is essential to the luminescence, which really accompanies the formation of the hydroxides of the metals from the oxide.

W. G.

Cause of the Sensitiveness of Chemical Compounds to Light. JOH. PLOTNIKOW (*Chem. Zeit.*, 1919, **43**, 321—323, 337—338).—A theoretical paper in which it is shown that photochemical reactions take place according to the schemes: (i) acids, $R \cdot CO_2H \rightarrow RH + CO_2$; (ii) aldehydes, $R \cdot COH \rightarrow RH + CO$; (iii) alcohols, $R \cdot CH_2 \cdot OH \rightarrow RH + CO + H_2$; (iv) ketones, $R \cdot CO \cdot R' \rightarrow R \cdot R' + CO$; (v) diazo-compounds, $RN_2R' \rightarrow R \cdot R' + N_2$. The illumination of a double bond leads either to the production of a stereoisomeride or an intramolecular change or the formation of a saturated closed ring system. Light has the tendency to convert unsaturated systems or compounds into systems stable to light. The production of stereoisomerides or intramolecular changes is to be regarded as the first intermediate stage of the action of light. Systematic photolysis and careful choice of the source of light will effect the above-named changes in all aliphatic compounds of the types mentioned. In these changes energy may be either absorbed or evolved. If there is no possibility of the formation of a more saturated or less saturated system, then a photo-equilibrium is set up which may be displaced in either direction by varying the wave-length of the light. The photochemical and photocatalytic properties of the elements are periodic functions of their atomic weights. J. F. S.

Limiting Absorption Frequencies of Röntgen Rays by the Heavier Elements particularly the Rare Earths. MANNE SIEGBAHN and EDV. JÖNSSON (*Physikal. Zeitsch.*, 1919, **20**, 251—256).—The limiting absorption frequency is absolutely characteristic of a chemical element, and therefore serves to identify and establish the purity of any given element. The present work was undertaken with the object of measuring this factor in the case of the rare earth metals. Various methods were available, but for various reasons were unsuitable; the methods due to de Broglie (A., 1916, ii, 509) and Wagner (*Bayr. Akad. d. Wiss.*, March, 1916) are associated with a fundamental error due to the penetration of the Röntgen rays into the crystals, whereby the reflection occurs deep in the crystal. The authors have developed a modification of this method. The light passes through a thick lead slit at the back of which the element in any of its compounds is placed;

thence the rays pass to a rock salt or calcite crystal 2 mm. thick, and are there reflected through a second slit which is fitted with gold edges, and thence through a third slit to the photographic plate. The apparatus is fitted up in a lead-lined cast-iron chamber. The Röntgen rays were produced from a glowing cathode tube. Measurements were made with the elements of atomic numbers 48—67, 78—83, 90, and 92. The following values were obtained: the atomic number is bracketed in each case: Cd (48), $\lambda = 1\cdot470$; Sn (50), $\lambda = 1\cdot537$; Te (52), $\lambda = 1\cdot606$; I (53), $\lambda = 1\cdot641$; Cs (55), $\lambda = 1\cdot706$; Ba (56), $\lambda = 1\cdot739$; La (57), $\lambda = 1\cdot772$; Ce (58), $\lambda = 1\cdot807$; Pr (59), $\lambda = 1\cdot843$; Nd (60), $\lambda = 1\cdot878$; Sa (62), $\lambda = 1\cdot948$; Eu (63), $\lambda = 1\cdot983$; Gd (64), $\lambda = 2\cdot018$; Dy (66), $\lambda = 2\cdot088$; Ho (67), $\lambda = 2\cdot125$; Pt (78), $\lambda = 2\cdot518$; Au (79), $\lambda = 2\cdot561$; Hg (80), $\lambda = 2\cdot601$; Tl (81), $\lambda = 2\cdot647$; Pb (82), $\lambda = 2\cdot687$; Bi (83), $\lambda = 2\cdot725$; Th (90), $\lambda = 2\cdot979$; and U (92), $\lambda = 3\cdot089$. The wavelengths are all given in Ångström units. The results are compared with those of de Broglie (*loc. cit.*), Wagner (*loc. cit.*), and Blake and Duane (*Phys. Rev.*, 1917).   J. F. S.

The Relation between the *L*-Series of *X*-Ray Spectra and the Atomic Weight. F. KIRCHOF (*Physikal. Zeitsch.*, 1919, **20**, 211—214).—The product of the *L*-wave-length into the square of the integer nearest approaching half the atomic weight (called Rutherford's ordinal number) is approximately a constant, equal to 12,550, for the elements from zinc to uranium.   F. S.

The Radioactivity of the Natural Gases of Canada. JOHN SATTERLY and J. C. MCLENNAN (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 153—160).—The authors have measured the amount of radium emanation per litre of gas and the helium and nitrogen content of a considerable number of natural gases of Canada. The results show that there is no direct relationship between the radioactivity and either the helium or the nitrogen content, but that helium and nitrogen usually vary together.   W. G.

The Radioactivity of Rubidium. OTTO HAHN and MARTIN ROTHENBACH (*Physikal. Zeitsch.*, 1919, **20**, 194—202).—The β-activity of rubidium preparations of various ages since preparation show no variation such as is to be expected if the β-rays arose from a relatively short-lived isotope of rubidium, and cannot be separated or affected by chemical purification. The radioactivity appears to be an atomic property of rubidium. The radiation from a plate 25 cm. in diameter, covered uniformly with the rubidium preparation, was compared with that of uranium from a similar surface of uranium oxide of about 0·5 mg. per cm.², α-rays being absorbed by passage through 0·01 mm. of aluminium foil. The soft β-rays of uranium-X_1, after subtracting the effect due to the penetrating β-rays of uranium-X_2, were half absorbed in 0·015 mm.

of aluminium ($\mu_{Al} = 463[\text{cm.}]^{-1}$). The β-rays of rubidium were exponentially absorbed, showing that they were homogeneous as regards velocity and penetrating power, being half-absorbed by 0·020 to 0·0225 mm. of aluminium ($\mu_{Al} = 347-308[\text{cm.}]^{-1}$), and are therefore somewhat the more penetrating. The soft β-rays given by radium itself have an absorption coefficient of 312(cm.)$^{-1}$ in aluminium. The velocity of the rubidium rays, estimated from their absorption coefficient, is 58 to 60% of that of light.

Under the conditions described, 12·6 grams of rubidium sulphate spread over 500 cm.^{2}, compared with a similar surface of 0·28 gram of uranium oxide, gave an activity per gram of rubidium salt 1/184th of that per gram of uranium oxide (total β-rays). Referred to the metals, the ratio is 1:139, and subtracting for the effect of the hard β-rays of uranium-X_2, the ratio is 1:32. By * using less and less rubidium salt and extrapolating to a film of zero thickness, the ratio is further increased in favour of the rubidium to 1:15, to an accuracy of 20%. That is, the β-activity of rubidium is 1/15th of that due to uranium-X_1 in the same weight of uranium, absorption in the material being corrected for. For thorium, the ratio is probably 1/10th, comparing similar β-rays.

Applying the law of radioactive change, the product of rubidium should be an isotope of strontium, and of potassium an isotope of calcium. The investigation of the atomic weight of calcium derived from potash felspar, containing only small amounts of calcium, is suggested, as if the calcium is a product of the potassium, its atomic weight should be about a unit less than the accepted value. The period of half-change of rubidium, calculated from the ratio of its β-activity to that of uranium-X_1, is about 10^{11} years, and for potassium probably three times as great. If the age of the oldest felspars is taken as 10^9 years, only 0·17% of the potassium should have changed into calcium. The period of potassium, however, may be as great as seven times that of rubidium, and it is doubtful if the expected difference of atomic weight would be detectable. Similarly for the possible case of cæsium transforming itself into barium, though no β-activity of cæsium has been detected, an examination of the cæsium mineral pollux is suggested.   F. S.

Is the Electrical Conductivity of the Elements Conditioned by the Presence of Isotopes ?   F. H. LORING (*Chem. News*, 1919, **119**, 14—16).—Assuming that those elements the atomic weights of which are not whole numbers are mixtures of two isotopes the atomic weights of which are whole numbers, it is suggested that the proportions of the two isotopes in the element may determine its electrical conductivity. It is further suggested that in those elements having a high conductivity there may be a greater proportion of the isotope of lower atomic weight, whilst in the non-conducting elements the proportions may be reversed. This idea is developed in a table, in which, for a number of conducting and non-conducting elements, the atomic weights and proportions of hypothetical isotopes are given.   E. H. R.

New Process for Measuring the Specific Inductive Power of Liquids.

FÉLIX MICHAUD and AHMED BALLOUL (*Ann. Physique*, 1919, [ix], **11**, 295—322).—The apparatus consists of a cylindrical condenser with a vertical axis, between the armatures of which the liquid rises under the action of the electric field, this rise being shown by a lowering of the level of the liquid in a lateral glass tube. The specific inductive powers of benzene, vaselin, *cyclo*-hexane, and turpentine were measured by this method, the results for benzene being 2·28 and for *cyclo*hexane 1·87. Solutions of phenol in benzene were also examined, and it was found that the dielectric constant reaches a maximum at a concentration of 11% of phenol. With mixtures, the phenomenon of "electro-osmosis" may occur, and it is proposed to study this in detail. The apparatus, slightly modified, may be used as an electrometer.

W. G.

Characteristics of the Spark Discharge and its Effect in Igniting Explosive Mixtures.

CLIFFORD C. PATERSON and NORMAN CAMPBELL (*Proc. Physical Soc. London*, 1919, **31**, 168—228).—The object of the work described in the paper was to determine the relationship between the electrical characteristics of a spark discharge and its power of igniting explosive mixtures. An attempt was made to produce a form of discharge in which the current and the duration of the discharge could be controlled and varied. This failed; the discharges obtained always consisted of a discontinuous series of individual sparks, each of which lasted for a time which could not be subdivided. Quantitative measurements show that each of these individual sparks consists in the passage of a definite quantity of electricity, Q, across the gap, and represents the discharge of a condenser of definite capacity previously charged to the spark potential of the gap. The maximum duration of a spark is of the order 0·00005 second, but there is reason to believe that the actual value is considerably less than this figure. It was found impossible to obtain a discharge which was continuous, except when it took the form of an arc or a brush. The sparks obtained from an induction coil are of the same type as those obtained from a condenser. It is therefore suggested that the quantity Q together with the form of the spark gap, may be sufficient to define the nature of the spark and to determine its igniting power. It is shown that discharges which consist of a series of similar sparks have the same igniting power as a single spark of the same character; that is to say, that the ignition, if it occurs at all. occurs at the first spark. Working with mixtures of petrol and air, it is shown that the igniting power of a spark increases with both the capacity discharging and the spark potential, but varies much more rapidly with the latter factor. The energy required for ignition decreases rapidly as the spark potential increases, and there is no indication that, if the spark potential were sufficiently increased, the energy required for ignition might not be reduced greatly beyond the measured limit, namely, 0·0004 joule. Other things

being equal, electrodes with small radius of curvature have greater
igniting power; the metal of which the electrodes is made is of no
importance from the point of view of ignition.   J. F. S.

The State of Super-conductivity in Metals. C. A.
CROMMELIN (*Chem. Weekblad*, 1919, **16**, 640—669).—A lecture
delivered before the Natuurkundig Gezelschap in Leiden. Special
reference is made to the work of Kamerlingh Onnes.   W. S. M.

Electromotive Activity of Carbon Monoxide. II. K. A.
HOFMANN and B. WURTHMANN (*Ber.*, 1919, **52**, [*B*], 1185—1194).—
It has been previously shown (this vol., ii, 8) that the oxidation
energy of carbon monoxide at the ordinary temperature can be
largely converted into electrical energy when the carbon monoxide
is oxidised at a copper electrode wetted with alkali hydroxide solu-
tion which is connected with a copper or platinum–air electrode.
It is now shown that, in contrast to hydrogen, the activity of carbon
monoxide is 0·12 volt greater at a copper than at a hydrogen elec-
trode, and, further, that the potential developed by the oxidation
of carbon monoxide is greater than that developed from hydrogen
by 0·3 to 0·08 volt. A copper electrode is particularly useful in
the utilisation of air in the carbon monoxide cell, since it forms a
primary oxide with the oxygen the oxidative power of which is
more than 0·2 volt greater than that of cupric oxide.

The potentials of the following cells are recorded, the electrolyte
being 15% pure potassium hydroxide solution in every case: $H_2|Pt$,
electrolyte, $HgO|Hg$, 0·93 volt at 22°; $CO|Pt$, electrolyte,
$HgO|Hg$, 0·91 volt; $CO|$coppered carbon, electrolyte, $HgO|Hg$,
0·96 volt at 17—18°; $CO|$coppered carbon, electrolyte, $Pb|$air,
1·17 volt at 14°; $CO|$platinised carbon, electrolyte, $Pt|$air, 1·05 volt
at 18°; $CO|Cu$, electrolyte, copper oxide$|$air, 0·95—0·99 volt at
20°; $CO|$platinised platinum, electrolyte, copper oxide$|$air, 0·91
volt at 18°; $H_2|$platinised platinum, electrolyte, copper oxide$|$air,
0·958 volt at 18·3°.   H. W.

Methods of Measuring Electric Cataphoresis. THE.
SVEDBERG and HUGO ANDERSSON (*Kolloid Zeitsch.*, 1919, **24**,
156—165).—The various methods which have been used for measur-
ing the migration velocity of colloidal particles in an electric field
are critically discussed and their errors enumerated. It is held
that none of the methods hitherto described is entirely satisfactory,
although that due to Linder and Picton (T., 1897, **71**, 568) is
usable in some circumstances. The authors describe the construc-
tion of a small vessel in which microscopic cataphoresis experiments
may be carried out with either direct or alternating current. A
photomicrographic method is described by which cataphoresis may
be measured by means of a direct current flowing for very short
periods. A microscopic method is also described in which altern-
ating current is used. A comparison of the results obtained by
these methods shows that the latter is more exact and gives values

which more nearly agree with the theoretical values than the former.   J. F. S.

Some Determinations of the Heat Conductivity of Selenium. EDNA D. SAYCE (*J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 356—363).—It was found that the thermal conductivity of selenium varied over a wide range, and was affected by the conditions which influence its electrical conductivity, and in the same direction, but in general to a slighter extent. The thermal conductivity of vitreous selenium at 25° was found to lie between 0·000293 and 0·000328. That of crystalline selenium at 25° varied from 0·00070 to 0·00183. The values for the crystalline form increased in general with the temperature of preparation, but diminished with age. In all the cases examined, the temperature coefficient was positive. All measurements were made with the selenium in darkness.   W. G.

The Determination of the Melting Points of Fats and Similar Substances by Means of the " Ascension " Method. D. J. DE JONG (*Pharm. Weekblad*, 1919, **56**, 925—931).—A short column of fat is allowed to solidify for twenty-four hours in a narrow glass tube open at both ends. The tube is placed vertically in water or glycerol so that the top of the fat column is below the level of the liquid. The temperature of the bath is raised slowly until the melting point is reached, at which temperature the column of fat begins to rise in the tube. Constant results were obtained when a thin-walled tube of 1 mm. internal diameter was used with a fat column 1 cm. long placed 1 cm. below the surface of the water.   W. S. M.

The Freezing Point of Solutions with Special Reference to Solutions Containing Several Solutes. CHARLES EDWARD FAWSITT (T., 1919, **115**, 790—801).

Cryoscopy in Acetylene Tetrabromide. R. LESPIEAU (*Compt. rend.*, 1919, **169**, 31—32).—Using benzene, chloroform, carbon tetrachloride, and ethyl ether as solutes, the author finds that the cryoscopic constant of acetylene tetrabromide, m. p. 0—0·13°, is 217, and that it varies but little with the nature of the dissolved substance or the concentration providing that the solution remains dilute.   W. G.

Variation of the Vapour Pressure with the Temperature. C. EMILIO CARBONELLI (*Gazzetta*, 1919, **49**, i, 151—153).—If θ denotes the absolute critical temperature of any liquid, π its critical pressure, and f its vapour pressure at a temperature T lying between absolute zero and the critical temperature, results in close agreement with the experimental data are given by the formula $\lg \pi/f = (\theta - T)/T . \lg h\theta/T$, h being a constant characteristic for each liquid. The values of $\lg h$ are: for carbon disulphide.

2·21503; chloroform, 2·58134; alcohol, 3·6765; water, 2·92714; ethyl ether, 2·80416; benzene, 2·64664; sulphur dioxide, 2·79064; cyanogen, 2·92481; and ammonia, 2·79.   T. H. P.

Maximum Vapour Pressures of Benzene and cyclo**Hexane at Moderate Temperatures and Calculation of their Principal Specific Heats.** G. DÉJARDIN (*Ann. Physique.*, 1919, [ix], **11**, 253—291).—A more detailed account of work already published (see this vol., ii, 95).   W. G.

The Saturated Vapour Pressures and the Heats of Vaporisation of Propyl Acetate at Different Temperatures. E. ARIÈS (*Compt. rend.*, 1919, **168**, 1188—1192).—Using the formula previously given (compare A., 1918, ii, 352) for calculating the value of the function Γ, from these results the author has calculated the saturated vapour pressures and heats of vaporisation of propyl acetate at different temperatures, and finds that the calculated values are in close agreement with those observed by Young.   W. G.

Volatility. OTTO RUFF (*Ber.*, 1919, **52**, [*B*], 1223—1238).—A theoretical paper in which the boiling point of the substance under atmospheric pressure is treated as a measure of its volatility. A series of tables is given showing the b. p. of fluorides, chlorides, hydrides, nitrides, and oxides as far as these have been determined. A discussion is then entered on with regard to the part played by mass, atomic volume, number of atoms in the molecule, negative minimal loading of the atoms in the molecule, and molecular symmetry on volatility. For details, the original paper must be consulted.   H. W.

Thermochemistry of Organic Fluorine Compounds. FRÉDÉRIC SWARTS (*J. Chim. Phys.*, 1919, **17**, 3—70).—Using a Langbein calorimetric bomb in which the silica-containing parts have been replaced by platinum, the author has determined the heat of combustion of a very large number of organic fluorine compounds. The results are recorded as (i) heat of combustion per gram, (ii) molecular heat of combustion (*a*) at constant pressure and (*b*) at constant volume. The heat of formation is also calculated in each case. The method of preparation, density, freezing point, and boiling point are recorded for every compound. By comparing the present results with those of Berthelot for other substances, the heat of substitution of one atom of fluorine for one atom of hydrogen is calculated. The substitution of the first atom of fluorine for hydrogen increases the heat of formation by about 17 cal., although the value fluctuates considerably for the various types of compounds: the introduction of the second atom of fluorine increases the heat of formation more than the first in all cases. The effect of substituting fluorine in benzene derivatives is also studied. It is shown that the replacement of one hydrogen

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atom by fluorine increases the heat of formation by 15·8 cal., but the second further increases it by 22·3 cal. if the second atom enters the para-position. The substitution of fluorine in mono-substituted benzenes increases the heat of formation from 8·15 cal. in the case of *o*-fluoronitrobenzene to 22·6 cal. in the case of *m*-fluorophenol. Similar calculations are made for tri- and tetra-substitution products of benzene.   J. F. S.

Heat of Coagulation. H. R. KRUYT and JAC. VAN DER SPEK (*Kolloid Zeitsch.*, ˙1919, **24**, 145—155).—The heat change occasioned by the sudden coagulation of arsenic sulphide sol and ferric oxide sol has been determined. In the case of arsenic sulphide, the coagulation was brought about by the addition of a solution of alum or potassium chloride. In all experiments, the heat change was extremely small, the amount of heat developed being 0·01—0·05 gram cal. per gram of arsenic sulphide. Ferric oxide sols were coagulated by the addition of sodium sulphate solution, and in this case the heat developed was considerably greater, amounting to 2 gram cal. per gram of ferric oxide. Experiments show that the heat developed depends very largely on the chlorine content of the sols. It is in keeping with expectation that there should be a considerable difference in the development of heat in the two cases, for the coagulation of ferric oxide sol is accompanied by a considerable increase in volume, whilst that of arsenic sulphide is accompanied by a very small diminution in volume. Further experiments were made to determine the heat change brought about by the adsorption of crystal-violet by animal charcoal. The results are only approximate and give the order of magnitude of the change; thus 5 grams of charcoal adsorb 2·21 millimols of crystal-violet with a heat absorption of 16·58 gram cals. For calculations of the amount of energy set free in the coagulation of arsenic sulphide sol, compare Linder and Picton (T., 1892, **61**, 114).   J. F. S.

Calculation of the Divergences from Avogadro's Law by the Method of Compressibilities. Application to Hydrogen Bromide. PH. A. GUYE (*J. Chim. Phys.*, 1919, **17**, 141—170).—A theoretical paper in which it is shown that the work of Moles (A., 1916, ii, 42, 526) and Reiman (A., 1917, ii, 137, 200) on the density of hydrogen bromide definitely indicates that the compressibility (pv) of this gas at $0°$ and at pressures above 1 atm. is not a linear function of the pressure (p) nor of the inverse of the volume $(1/v)$. This being the case, the product pv ought to be represented by a formula of the second degree of p or $1/v$, and this equation ought to hold for all gases less volatile than carbon dioxide. By means of the modified van der Waals's equation, it is known at once whether a gas ought to be represented in the neighbourhood of 1 atm. by an equation of the first or second degree. The use of a formula of the second degree, $(pv) = 1 + a + ap + bp^2$, or $(pv) = 1 + a^1 + a^1/v + b^1/v^2$ for the extra-

polation of the limiting value $(pv)_0$ which enters into the expression, giving the divergences from Avogadro's law, is justified by consideration of the best established equations of state. Two methods are indicated for calculating the constants of the preceding equations, and when these are applied to the results of Moles and Reiman (*loc. cit.*), the following values are obtained for hydrogen bromide at $0°$: (i) divergence from the law of Avogadro: $(1 + \lambda) = (pv)_0/(pv)_1 = 1.00934$; (ii) divergence of the compressibility between 0 and 1 atm.: $A^1_0 = 0.00925$. The experiments of Moles and Reiman lead to the same results. The methods adopted in these calculations are discussed at some length in the paper.

J. F. S.

Investigation of Poisson's Ratio by Means of the Gaseous Volume and Specific Heat at Low Temperatures. RUDOLF MEWES (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1918, **10**, 93; from *Chem. Zentr.*, 1919, i, 505).—A formula has previously been developed whereby the specific volumes of gases can be estimated from observation on the specific heats $k = c_p/c_v$ and c_p at low temperatures. The ratio v_{15}/v_t and v_0/v_t has been calculated from the formulæ $v_{15}/v_t = (1 + a)^{-t}$ and

$$v_{15}/v_t = v_{15}/[A t(c_p - c_p/k)/P + v_{15}]$$

and introduced into Poisson's equation. Since the calculated and experimental results are not in harmony, Poisson's equation does not appear to hold good. H. W.

Gaseous Volumes at Low Temperatures. RUDOLF MEWES (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1918, **10**, 81—82; from *Chem. Zentr.*, 1919, i, 505).—Theoretical considerations based on a table which gives the necessary data for helium, hydrogen, nitrogen, oxygen, air free from carbon dioxide and carbon monoxide, show that Gay-Lussac's law is not approximately obeyed at low temperatures (at about $-192°$), and that the most accurate observations yet made are vitiated by some error which is not yet explained. H. W.

Modification of Victor Meyer's Vapour Density Apparatus. GIOVANNI ROMEO (*Gazzetta*, 1919, **49**, i, 172.-174).— In this apparatus, the upper, narrow, tubular part above the bulb in which the substance is vaporised is considerably shortened, and round it is wrapped, in the form of a spiral, the tube through which the displaced air passes to the graduated measuring tube. The lower end of this spiral tube is connected with the top of the bulb, whilst the upper end emerges through the stopper of the jacket containing the heating vapour. In this manner, the apparatus is made shorter and more easily manipulated, less time is required for the uniform heating of the apparatus, and condensation of the vaporised substance on the cool parts of the apparatus is entirely avoided. T. H. P.

The Adsorption of Helium by Charcoal. STUART McLEAN (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 79—81).—A very

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small amount of helium is adsorbed by charcoal at the temperature of liquid air, the amount adsorbed being apparently independent of the volume of helium introduced into the apparatus.   W. C.

An Apparatus for Studying the Dissociation of Carbonate Rocks. G. A. BOLE (*J. Amer. Ceram. Soc.*, 1919, **2**, 410—417). —The dissociation of carbonate rocks may be studied by heating 0·1 gram of the sample in a modification of Victor Meyer's vapour density apparatus, consisting of a small platinum bucket which fits over the lower end of the porcelain sheath of a thermocouple and is held in place by a small porcelain wedge. The thermocouple is then placed in a tube of fused silica, 25 cm. long and 1·25 cm. in diameter, provided with a side-tube leading to a pneumatic trough and gas burette. The top of the silica tube is closed with a ground-glass stopper, into which are fused the wires of the thermocouple. The stopper also contains a glass tube carrying a stopcock. The lower part of the silica tube is surrounded by an electric furnace. The temperature of the sample is raised to about 450°, with the stopcock open to expel any moisture. The stopcock is then closed, the temperature raised steadily, and the volume of gas evolved is measured at regular intervals of time until the dissociation is complete. The gas is examined for carbon monoxide, and, if this is found, a fresh portion of the sample is treated for removal of organic matter, and a fresh determination of the dissociation temperature is then made. It is necessary to make a blank test in order to ascertain the expansion of the air in the apparatus at various temperatures and to correct the volume of gas accordingly. The same apparatus may be used for determining the temperature at which the dissociation pressure is just above that of the atmosphere by maintaining it at the highest temperature at which gas is evolved. In determining the rate of dissociation, 0·5 gram of the sample is placed in a small platinum bucket in the neck of the apparatus, the silica tube is heated to about 50° above the temperature at which the determination is to be made, the temperature allowed to fall slowly to the desired temperature and maintained constant for about fifteen minutes. The bucket is then released and allowed to fall to the bottom of the tube, and the gas evolved is measured after a definite interval of time. A series of determinations is made at increasingly higher temperatures, and the results are plotted. The apparatus may also be used to determine the carbon dioxide associated with lime and magnesia respectively in limestone and dolomite by raising the temperature to 750° while the sample is in the neck of the tube, then releasing the bucket, raising the temperature to 900°, and measuring the gas evolved at each temperature. The apparatus is simple, easy to use, rapid, and accurate. Organic matter, occluded gases, and moisture may be driven off by manipulating the stopcock immediately before making a determination.   A. B. S.

Piezo-chemical Studies. XV. Experimental Proof of Braun's Law. ERNEST COHEN and A. L. TH. MOESVELD (*Zeitsch. physikal. Chem.*, 1919, **93**, 385—515. Compare A., 1917, ii, 566). —With the object of ascertaining experimentally the extent to which Braun's law is true, the authors have determined (i) the temperature-coefficient of the solubility of *m*-dinitrobenzene in ethyl acetate, (ii) the pressure-coefficient of the solubility, (iii) the fictitious volume change, and (iv) the fictitious heat of solution of the same pair of substances (see A., 1918, ii, 297). These values when obtained were substituted in the expression

$$(dx/d\pi)_T : (dx/dT)_\pi = -T\Delta V / Q,$$

and the value of Q obtained and compared with the experimentally determined value of Q. In the expression above, $(dx/d\pi)_T$ is the pressure-coefficient of the solubility at constant temperature, $(dx/dT)_\pi$ the temperature-coefficient of the solubility at constant pressure, ΔV the fictitious volume change, that is, the volume change when a fixed amount of substance dissolves in an infinitely large volume of solvent at the temperature T, and Q the fictitious heat of solution. The value of Q found by this equation is $21\cdot07\pm0\cdot10$ gram cal./gram, whereas the experimental value of Q is $21\cdot02\pm0\cdot02$ gram cal./gram. From these figures, it is concluded the Braun law holds within the limits of experimental error. The solubility of *m*-dinitrobenzene in 100 grams of ethyl acetate is found to be 21·80 grams at 0·02°, 23·35 at 2·48°, 24·92 at 5·00°, 26·62 at 7·50°, 28·55 at 10·00°, 30·66 at 12·50°, 32·95 at 15·00°, 35·45 at 17·50°, 38·20 at 20·00°, 41·20 at 22·50°, 44·60 at 25·00°, 48·38 at 27·50°, 52·53 at 30·00°, 57·24 at 32·50°, and 62·32 at 35·00°. Calculating from these figures, the temperature-coefficient at 30·00° is found to be $0\cdot5653\pm0\cdot0007$ gram mols. per 100 mols. of solution per degree, or $0\cdot755\pm0\cdot001$ gram per 100 grams of solution per degree. An apparatus is described whereby the solubility under various pressures may be determined. Using this apparatus, the solubility of *m*-dinitrobenzene in ethyl acetate is determined at 30° under pressures 0, 100, 220, 300, 380, and 480 atmospheres, and from the results the pressure-coefficient of the solubility calculated to $(dx/d\pi)_{\pi=1} = -0\cdot00867\pm0\cdot00003$ mol. %/per atm., or, if $c=$weight %, $(dc/d\pi)_{\pi=1} = -0\cdot01161\pm0\cdot00005$ weight %/per atm. The specific volume of various solutions of *m*-dinitrobenzene in ethyl acetate has been determined at temperatures between 20·00° and 30·00° by means of an Ostwald-Sprengel pyknometer, and also by a dilatometric method. From the results, it is shown that $v_c=0\cdot96978$, that is, the specific volume of a solution saturated at 30·00° and 1 atm. pressure. The specific volume of solid *m*-dinitrobenzene at 30·00° was determined by a dilatometric method, using water as the liquid, and the value 0·63872 found. From the data thus accumulated, the fictitious volume change is calculated, and the values $0\cdot0442\pm0\cdot0001$ c.c./gram and $7\cdot392\pm015$ c.c./mol. obtained. A long description of the method of experimentally obtaining the fictitious heat of solution is given, and from the experiments the value $21\cdot02\pm0\cdot025$ gram cal./per

gram, or 3534 ± 5 gram cal./per mol., obtained. The paper ends with a long and detailed criticism of a paper on the same subject by H. F. Sill (A., 1917, ii, 75).   J. F. S.

Liquid Crystals and Anisotropic Liquids. D. VORLÄNDER (*Zeitsch. physikal. Chem.*, 1919, **93**, 516—520).—Polemical against Baur (*Jahrb. Chem.*, 1916, **25**, 362), Bose (A., 1907, ii, 443; 1908, ii, 1017), Nernst (*Lehrb. theoret. Chem.*), and Herz (*Moderne Probleme allgem. Chem.*). The author protests against the views put forward by the authors named, that liquid crystals are heterogeneous substances consisting of a disperse phase and a dispersion medium.   J. F. S.

Orientation of Anisotropic Liquids on Contact with Crystals. II. F. GRANDJEAN (*Bull. Soc. franç. Min.*, 1917, **40**, 69—105; from *Chem. Zentr.*, 1919, i, 498—499. Compare A., 1917, ii, 451).—The author describes the behaviour of the same crystals which were previously used with five new anisotropic liquids, *p*-azoxyanisolephenetole, dibenzylidenebenzidine, *p*-ditolylidenebenzidine, methoxycinnamic acid, and *p*-anisylideneaminoazotoluene. Orientation occurs in ninety cases out of a hundred, and hence is a general property. The crystal surface causes a peculiar field of force, the nature of which is not explained. It orientates anisotropic liquids in such a manner that their axes can assume one or more definite positions, which are termed equilibrium or field directions. One of these is perpendicular to the face of the crystal. If the latter corresponds with a net plane of high density, there is generally one or more of these directions parallel to the face. With respect to behaviour on change of temperature, three types are to be considered, in which (i) the orientation is not greatly altered, (ii) a well-defined orientation suddenly passes into a second arrangement, and (iii) the orientation changes gradually with changing temperature.   H. W.

Periodic Precipitation. (MISS) A. W. FOSTER (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 55—57).—The addition of one drop of a 1% solution of silver nitrate to a thin sheet of gelatin impregnated with potassium chromate produced precipitation in the form of Leisegang's rings. When a colloidal copper solution was used instead of water for making the gelatin plate, the precipitate was not in the form of rings, but as microscopic quantities scattered over the plate. Similar experiments were performed, agar being used instead of gelatin, and it was found that in this case the presence of the positively charged copper particles did not change the character of the precipitate.   W. G.

Rhythmic Solidification. D. VORLÄNDER and ILSE ERNST (*Zeitsch. physikal. Chem.*, 1919, **93**, 521—526).—Solutions on evaporation in many cases deposit crystals in a rhythmic manner. This phenomenon is particularly well observed in the crystallisation of an aqueous solution of 5-nitrophenyl-2-glycine-1-carboxylic acid;

this substance crystallises in open vessels in a series of rings, the formation of which is connected with the surface tension and the adhesion of the solution on the vessel walls, and is also due to the fact that after the deposition of the first crystals the solution is drawn by capillary attraction to the crystals. As the evaporation proceeds, the surface tension of the solution overpowers the adhesion and capillary attraction, so that the solution withdraws itself spasmodically from the edges of the dish. In the case of molten substances, the authors have found very few substances which solidify rhythmically, but this phenomenon is well shown by the ethyl ester of p-ethoxybenzylideneaminophenylpropionic acid. This substance, which was prepared by the method described by Beilstein and Kuhlberg (Annalen, 1872, **163**, 162), melts at 59° to an amorphous liquid; on supercooling the molten substance to 34°, it forms liquid crystals. The rhythmic solidification occurs when either of the liquid forms passes into the crystalline solid, and takes place as follows: When a few drops of the molten substance are placed on a clean glass plate, a small, round, crystalline mass first forms; this exerts a capillary attraction on the surrounding liquid, and the liquid rises in the crystal mass and solidifies on top of it, and also on the sides, whilst the level of the liquid falls. Then a period of no growth of the crystal height sets in, because the adhesion of the liquid to the glass plate has overpowered the capillary attraction, but at the same time the crystal mass begins to grow rapidly from the sides until a quantity of liquid is held in the crystal network, when the side growth ceases and the vertical growth recommences. These three processes then repeat themselves in the same order. Photomicrographs illustrating the crystallisation in this case are appended to the paper.   J. F. S.

New Method of Weighing Colloidal Particles. E. F. BURTON (Proc. Roy. Soc., 1919, [A], **95**, 480—483).—A preliminary paper in which it is shown that by superimposing on a colloidal particle the motion produced by an electrical field on that produced by gravitation, colloidal solutions which possess particles too small to settle under the influence of gravity alone may be made to settle. The experimental procedure consists in superimposing on a colloidal solution contained in a migration tube a small column of conductivity water of the same specific conductivity as the colloidal solution. The position of the interface between the two liquids is noted, and a current of E.M.F. ca. 100 volts is passed for ten minutes, reversed, and again passed for ten minutes. The position of the interface is noted at the moment of reversal and at the end of the experiment. In the first period of ten minutes, the motion of the particles is due to a force $Xe + mg$ and in the second ten minutes to $Xe - mg$. From these values, the equation $a^2 = 9/2 . nv/(\rho - \rho^1)g$ is deduced, in which a is the radius of the particle, v the velocity under the influence of gravitation, ρ and ρ^1 the densities of the particle and medium respectively, n the viscosity of the solution, and g the gravitational force. By

this method, colloïdal particles of silver were found to have a radius $2 \cdot 2 \times 10^{-5}$ cm., whereas $1 \cdot 7 \times 10^{-5}$ was obtained by the counting method. The velocity v was $8 \cdot 3 \times 10^{-5}$ cm. per sec.

J. F. S.

Colours of Colloids. V. Metallic and Vitreous Lustre. WILDER D. BANCROFT (*J. Physical Chem.*, 1919, **23**, 289—347).— A continuance of the discussion on colour phenomena dealt with in previous papers (A., 1918, ii, 102; this vol., ii, 187, 275). In the present paper, metallic and vitreous lustre as it affects colour is discussed in connexion with minerals, feathers, and beetles.

J. F. S.

Emulsification of Water and of Ammonium Chloride Solutions by Means of Lamp Black. WILLIAM C. MOORE (*J. Amer. Chem. Soc.*, 1919, **41**, 940—946).—Weighed quantities of lamp black, both the commercial article and that previously extracted with benzene, were stirred for measured times with petroleum (D^{15} 0·8149) and water or solutions of ammonium chloride of known concentration. The emulsions thus obtained, in which petroleum was the continuous phase, were examined under a micrometer microscope, and the diameter of the aqueous drops measured. The experiments show that various samples of lamp black have widely differing emulsifying properties. With a large quantity of lamp black, smaller emulsified drops of water are obtained in petroleum than when less lamp black is used. Water wets commercial lamp black less readily than the extracted lamp black. Ammonium chloride in normal solution wets the commercial lamp black more readily than the purified substance. Water wets purified lamp black more readily than does ammonium chloride solution, the converse being the case for the commercial lamp black. The drops of emulsified water become larger the greater the concentration of the ammonium chloride, owing to the increasing surface tension of the ammonium chloride solution. The effect of changing the time of stirring is somewhat indefinite; a tendency is shown for the size of the drops to pass through a minimum as the time is increased.   J. F. S.

Electromagnetic Hypothesis of the Kinetics of Heterogeneous Equilibrium, the Structure of Liquids and Cohesion. WILLIAM D. HARKINS and H. H. KING (*J. Amer. Chem. Soc.*, 1919, **41**, 970—992).—A theoretical paper in which an hypothesis is developed that the distribution of a solute between various phases and interfaces is conditioned by the intermolecular electromagnetic fields. Cohesion is considered to be due to these fields, and is explained on the basis of the valency theory of Lewis (A., 1916, ii, 310) as being due to intermolecular fitting of electrons in the outer shells of atoms. The constant surface film of butyric acid on the surface of water is found to contain $2 \cdot 78 \times 10^{14}$ molecules, whilst if benzene covers the water phase, the layer contains

2.79×10^{14} molecules per sq. cm. Thus the presence of benzene does not affect the number of molecules in the film. A theory of solubility and of thermodynamic environment is developed, and an hypothesis is made to explain the variation of the fugacity or thermodynamic potential of a component, with variations in its environment. In this connexion, solubility, Raoult's law, melting point, compressibility, coefficient of expansion, latent heat of vaporisation, adsorption, and surface structure are discussed. The theory is complicated, and the original should be consulted for details.   J. F. S.

Chemical Affinity. FRITZ EPHRAIM (*Naturwiss.*, 1919, **7**, 49—55; from *Chem. Zentr.*, 1919, i, 409—410).—The energy of a reaction is, in general, the sum of the energies of a number of component reactions, and therefore gives little information about the latter. The energy of analogous reactions is best studied with closely related compounds, whereby the common side-reactions are most readily eliminated. In this manner, the relative affinity of water of crystallisation to different molecules is conveniently determined by investigation of substances such as the alums. Studies of this nature are best effected by estimation of the affinities of subsidiary valencies with hydrates, and particularly ammines. The gaseous nature of ammonia allows the thermochemical investigation to be replaced by determination of the dissociation temperature, that is, the temperature at which the pressure of ammonia is equal to the atmospheric pressure. The affinity of ammonia for the molecule in question is obviously greater as the dissociation temperature is higher. The following compounds have been compared in this manner: $NiI_2,6NH_3$, $CoI_2,6NH_3$, $FeI_2,6NH_3$, $MnI_2,6NH_3$, $ZnI_2,6NH_3$, $CdI_2,6NH_3$. The temperature of decomposition decreases with increasing atomic volume, and the product of dissociation temperature and atomic volume is approximately constant. Consequently, the dissociation temperature can be calculated if that of a similar substance and the atomic volume of the metal are known, and, conversely, unknown atomic volumes can be calculated from the observed dissociation temperature. Irregularities are only observed with cadmium. When compounds of a metal with different acid radicles are investigated, the size of the latter appears to be important, but its effect can only be estimated with difficulty, since, in complex radicles, only that portion which is closely related to the metallic atom should be considered. The affinity for neutral molecules is particularly marked with large acid radicles. The relationships are most favourable when the metal is surrounded by acid radicles, as in the case of a multivalent metal united to several univalent radicles. With increase in volume of the neutral molecules, as with transition from ammonia to alkylamines, the affinity decreases. With complex cations, the neutral portion is more firmly bound as the size of the metal decreases. Conversely, the stability of complex ions increases with increasing volume of the metal. Systematic investigation of the

stability of a group of complex compounds permits the decision as to whether the complex is united to the anion or cation, and thus allows a determination of constitution in solid substances. The method is, in principle, applicable to all dissociable compounds. From this point of view, an explanation is given of the fact that the capacity of neutral salts to cause the separation of amino-acids is reversed by addition of traces of acid or alkali. The formation of dissociation equilibria is in many respects analogous to the evaporation of a liquid. The absolute boiling points under the same pressure of chemically related substances stand to one another in a constant ratio. The boiling-point rule can also be used as dissociation rule, as is shown in the case of the ammines of the iodides previously described. The rule is also true for substances of widely differing chemical nature. The calculation of the dissociation temperature for any pressure is therefore possible when it is known at any definite pressure. The limits of existence of compounds can therefore be defined.   H. W.

Fission of Acid Salts in Aqueous Solution into Normal Salts and Free Acids. W. DIECKMANN and ALBIN HARDT (*Ber.*, 1919, **52**, [*B*], 1134—1142. Compare Thoms and Sabalitschka, A., 1917, i, 700; Sabalitschka, this vol., ii, 282; McCoy, A., 1908, ii, 466; McCoy and Chandler, A., 1908, ii, 467).—It has been previously shown that dibasic organic acids can be partly extracted from aqueous solutions of their acid salts by treatment with ether, and McCoy has based a method of estimating the ratio of the first and second dissociation constants of such acids on this fact. The authors have repeated Chandler's work with camphoric and fumaric acids, and confirm his results. They have also applied the method to the determination of the second dissociation constant of homo-phthalic acid ($10^6 k_1 = 191$), and obtained the value $k_1 : k_2$ 212 (for $c = 0.001$), and therefore the value $10^6 k_2 = 0.9$. When contrasted with glutaric acid, which also contains the carboxyl groups in the 1 : 3-position ($10^6 k_1 = 47.4$, $k_1 : k_2 = 14$, $10^6 k_3 = 3.38$), the ratio $k_1 : k_2$ appears greatly increased, and here, as in other cases, to be subject to constitutive influences as well as to those due to the relative position of the carboxyl groups. Experiments with benzylmalonic acid and β-phenylglutaric acid show that the ratio of the constants, in comparison with those of the parent substances, is not greatly affected by the entry of a substituent in the symmetrical position. Comparison of δ-keto-β-phenyladipic acid,

$$CO_2H \cdot CH_2 \cdot CHPh \cdot CH_2 \cdot CO \cdot CO_2H$$
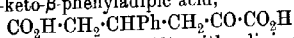
($10^6 k_1 = 9300$, $k_1 : k_2 = 850$, $10^6 k_2 = 11$), with adipic acid ($10^6 k_1 = 37.6$, $k_1 : k_2 = 15.7$, $10^6 k_2 = 2.4$) shows a considerable increase in the first dissociation constant which can with certainty be ascribed to the presence of the carbonyl group; in addition, both the ratio $k_1 : k_2$ and k_2 are increased, which is not in accordance with Smith's rule (A., 1918, ii, 155) that a substituent has an unlike influence on the two carboxyl groups.

The statement of Thoms and Sabalitschka (*loc. cit.*) that phthalic

acid can be extracted by ether from aqueous solutions of its normal sodium salt could not be confirmed, nor do the authors find that phthalic acid suffers partial dehydration when its ethereal solution is evaporated on the water-bath.   H. W.

Chemical Processes in Solution and their Velocity. MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1919, **106**, 149—188).—A purely mathematical paper in which the theory of gas reactions (compare A., 1918, ii, 151) is discussed in relation to the quantum theory and is applied to reactions in solution. Owing to the nature of the paper, satisfactory abstraction is impossible, but it may be stated that it is found that the integration constant of the reaction velocity in solution is identical with that in gases.
                                                    E. H. R.

The Law of Action of Sucrase : Influence of Viscosity on the Velocity of Hydrolysis. H. COLIN and (MLLE.) A. CHAUDUN (*Compt. rend.*, 1919, **168**, 1274—1276. Compare A., 1918, i, 414; ii, 357).—The authors show that the velocity of hydrolysis of sucrose, the amount of sucrase remaining constant, is directly proportional to the fluidity of the solution. The ratio dV/dF, for solutions of varying sucrase content, is proportional to the amount of sucrase present for a given sucrose concentration.
                                                    W. G.

The Hydrolysis of Ethyl Acetate. L. BERCZELLER (*Oesterr. Chem. Zeit.*, 1919, **22**, 66—67).—The hydrolysis of ethyl acetate by hydriodic, hydrobromic, hydrochloric, and nitric acids has been studied with the object of determining the effect, if any, of the anion on the rate of the reaction. For each experiment, 10 c.c. of $N/2$-ethyl acetate solution were mixed with 1, 2·5, 5, 10, or 40 c.c. of $N/2$-acid solution and allowed to remain for times varying from a quarter of an hour to twenty-eight hours, at the end of which time the solution was titrated with $N/5$-potassium hydroxide. The rates of hydrolysis are not equal for the different acids, the strengths of the acids being in the order $HI > HBr > HCl > HNO_3$. It is thus shown that in this typical case of catalysis the effect is not confined to the hydrogen ion, the chemical nature of the anion having the same influence here as in the so-called neutral salt action. The presence of iodine in the hydriodic acid was found to have a retarding influence on the reaction.   E. H. R.

Definition of the Terms : Explosion, Explosive Action, Thermite. A. LANGHAUS (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1918, **13**, 310—313; from *Chem. Zentr.*, 1919, i, 692—693. Compare this vol., ii, 219).—The definitions given in the literature lay stress on the function of gaseous factors in explosive decomposition and scarcely mention the importance of chemical decomposition, to which the author attributes prime importance, since actual explosions and explosive actions can be distinguished by it. The

following definitions only take into account the nature of the reaction; a definition in the strict physicochemical sense will be given later.

True explosion is the chemical decomposition of a substance in a definite manner which is distinguished by development of heat (chemical importance), sound (physical importance), and destruction of the immediate surroundings in consequence of high velocity of decomposition (technical importance). In decomposition of this kind, gases, either pre-formed or generated, are the chief agents. (1) *Direct Gas Explosions.*—The pre-formed gases are the actual carriers of the explosion, whilst the gaseous products cause the external physical and technical effects; the explosion may be total, as with oxyhydrogen gas, or partial, as with gas and solid or liquid substance, as in the cases of dust explosions, ether, and petroleum explosions. (2) *Indirect Gas Explosions.*—The gases do not react chemically and are not the carriers of the actual explosion, but merely cause the physical and technical effects. Two cases are to be distinguished, in the first of which a gas is present in which the solid or liquid substance explodes (silver acetylide, aluminium, or magnesium with an oxygen carrier, potassium chlorate and antimony sulphide, percussion gases), whilst in the second class the gas is generated by decomposition of solid or liquid substances (true explosives, such as nitroglycerol, gunpowder, picric acid). The substances capable of such decomposition are termed explosive substances.

Explosion-like actions are such as show external characteristics similar to those outlined above, but do not involve chemical action. With gaseous substances, gas may be pre-formed (lightning in air, explosion of bombs filled with compressed gas) or may be generated (boiler explosions, quicklime and water in a closed vessel); with liquids, such action is observed in the case of vessels filled with liquid, and examples with solids are afforded by Rupert's drops and explosive antimony.   H. W.

Emission Spectra and Atomic Structure. JOHN WILLIAM NICHOLSON (T., 1919, 115, 855—864).—A lecture delivered before the Chemical Society on March 6th, 1919.

The Quantum Theory and New Theories of Atomic Structure. JAMES HOPWOOD JEANS (T., 1919, 115, 865—871). —A lecture delivered before the Chemical Society on May 1st, 1919.

Arrangement of Electrons in Atoms and Molecules. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1919, 41, 868—934).— A theoretical paper in which a theory of the arrangement of electrons in atoms and molecules is put forward; this theory is essentially an extension of Lewis's theory of the cubical atom (A., 1916, ii, 310). The electrons in atoms are either stationary or rotate, revolve or oscillate, about definite positions in the atom.

In the most stable atoms, namely, those of the inert gases, the electrons have positions symmetrical with respect to a plane (equatorial plane) passing through the centre of the nucleus of the atom. No electrons lie in the equatorial plane. There is an axis of symmetry (polar axis) at right angles to this plane through which four secondary planes of symmetry pass, forming angles of 45° with each other. These atoms have the symmetry of a tetragonal crystal. The electrons of any atom are distributed through a series of concentric, nearly spherical shells, all of equal thickness. The mean radii of the shells are in the ratio $1:2:3:4$, and the effective areas are in the ratio $1^2:2^2:3^2:4^2$. Each shell is divided into cellular spaces or cells occupying equal areas and symmetrically distributed over the surface of the shell. The first shell contains 2 cells, the second 8, the third 18, and the fourth 32. Each cell in the first shell can contain only one electron, but every other cell can contain either one or two electrons. The inner cells must have their full quota of electrons before the outside shell can contain any. No cell in the outside shell can contain two electrons until all other cells in this layer contain at least one. The electrons in the same cell neither repel nor attract one another, which implies a magnetic attraction that overcomes the electrostatic repulsion. When the number of electrons in the outside layer is small, the arrangement of the electrons is determined by the magnetic attraction of the underlying electrons, but when the number of electrons increases, especially when the layer is nearly complete, the electrostatic repulsion to the underlying electrons and of those in the outside shell becomes predominant. The properties of the atom are determined primarily by the number and arrangement of electrons in the outside shell and by the ease with which the atom is able to revert to more stable forms by giving up or taking up electrons. The stable and symmetrical arrangements of electrons corresponding with the inert gases are characterised by strong internal and weak external fields of force. The smaller the atomic number, the weaker the external field. The most stable arrangement of electrons is that of the pair in the helium atom. A stable pair may also be held by (a) a single hydrogen nucleus; (b) two hydrogen nuclei; (c) a hydrogen nucleus and the kernel of a second atom; (d) very rarely by two atomic kernels. The next most stable arrangement of electrons is the octet, that is, a group of eight electrons like that in the second shell of the neon atom. Any atom with atomic number less than 20, which has more than three electrons in its outside layer, tends to take up enough electrons to complete its octet. Two octets may hold one, two, or three pairs of electrons in common. One octet may share one, two, three, or four pairs of its electrons with one, two, three, or four other octets. One or more pairs of electrons in an octet may be shared by the corresponding number of hydrogen nuclei. No electron can be shared by more than two octets. This theory explains the periodic properties of all the elements, including those of the eighth group and the rare earths.

It accounts for the magnetic and physical properties as well as the chemical properties. It leads to a simple theory of valency for both polar and non-polar substances. It explains the structure of compounds, which, according to Werner's theory, are second-order compounds with a co-ordination number equal to four. According to the present theory, such compounds are to be regarded as typical primary valency compounds. This valency theory is based on the equation $e = 8n - 2p$, where e is the total number of available electrons in the shells of all the atoms in a molecule, n the number of octets forming the outside shells, and p the number of pairs of electrons held in common by the octets. The theory leads to definite conceptions of the positions of the electrons in the molecules or space lattices of compounds. The structures of the molecules of nitrogen, carbon monoxide, hydrogen cyanide, and nitric oxide are exceptional, because the kernels of both atoms are contained within a single octet. This accounts for the practically identical physical properties of nitrogen and carbon monoxide and for the abnormal inertness of nitrogen.   J. F. S.

The Derivation of the Periodic System of the Chemical Elements from the Electron Theory. HEINRICH TEUDT

(*Zeitsch. anorg. Chem.*, 1919, **106**, 189—208).—Starting with the conception of the atom as a positively charged nucleus surrounded by rotating negative electrons, the author shows how many of the important properties of the periodic system of the elements follow from this conception. Two kinds of electrons are distinguished, an inner sphere firmly held by the attractive force of the positive nucleus and an outer sphere of valence electrons, through which combination with other atoms takes place. The rotating electrons are probably distributed symmetrically on spherical surfaces as near the equatorial zone of the atom as possible. Hydrogen is the only element which has only valence electrons, since its one electron functions in this manner. The two electrons of helium are both bound in the inner sphere, the element having no valence electrons, and the same is true of the other inert gases. The remaining elements have electrons of both kinds. Those of the first horizontal series have two electrons in the inner sphere, whilst the number of possible valence electrons increases from lithium (1) to fluorine (7). Some of the valence electrons tend to be retained in the inner sphere, however, for instance, when carbon becomes bivalent, nitrogen tervalent, oxygen bivalent, and fluorine univalent. In the second horizontal series, the inner sphere contains at least ten electrons, in the third series eighteen, and so on.

The metals are distinguished from the metalloids by their more mobile or less firmly held valence electrons. Passing from left to right in a horizontal series, the number of positive charges on the nucleus steadily increases, whilst the number of inner electrons remains constant, and in order to retain their position the latter must increase their centrifugal force by increasing their rotation velocity. At the same time, the valence electrons must increase

their rotation velocity to a corresponding degree to prevent disruption of the atom, and the whole electron system becomes more stable. It follows that the metalloid character of the elements increases from left to right of a horizontal series. In the third, fifth, and seventh horizontal series, however, the metallic character is maintained throughout. To explain this irregularity, it is supposed that in these series the inner sphere is made up of an odd number of rings of electrons, the central ring occupying the equatorial position. This central ring of electrons intercepts lines of force which, in the case of the second, fourth, and sixth series with even numbers of rings of electrons in the inner sphere, would serve to hold the valence electrons with greater force. It follows that the outer electrons of odd series are more mobile than those of the even series, and the elements of the former are therefore more metallic. The appearance of the iron, ruthenium, and osmium triads is attributed to the relative instability of the electron systems developed at the end of the third, fifth, and seventh horizontal series. The elements copper, silver, and gold are closely related to the respective triads which they follow, and should not be placed in Group I. As the number of electrons in the atom increases, the forces retaining the valence electrons become weaker, and consequently the metallic character of the elements becomes more marked with increasing atomic weight. The periodic progression of the atomic volumes of the elements is discussed in terms of the electron theory.   E. H. R.

A New Periodic Classification of the Chemical Elements.
MARC CHAUVIERRE (*Bull. Soc. chim.*, 1919, [iv], **25**, 297—305).—
Marking off the atomic weights as abscissæ and the principal valencies of the elements (from zero to four) as ordinates, a periodic curve the period of which is double is obtained, the elements of the iron, palladium, didymium, and platinum families, the atomic weights of which are close together, being placed above the level of quadrivalency. The elements which occur in the same periodic position on the curve have generally similar chemical properties and correspond with the natural groups of elements. The elements may also be arranged by this method in a table similar to that of Mendeléev.   W. G.

Annual Report of the International Committee on Atomic Weights (T., 1919, **115**, 879—885).

The Alchemists Known as Hollandus. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1919, **43**, 265—267, 286—288, 301—303). —In a long contribution to the discussion on the authenticity and period of Jan Isaac and Isaac of Holland, the author maintains his original view (A., 1916, ii, 525) against the criticism of Schelenz (A., 1917, ii, 529).   E. H. R.

Basil Valentine. B. NEUMANN (*Zeitsch. angew. Chem.*, 1919, **32**, I, 184).—Polemical. A reply to Hommel (this vol., ii, 224).
S. S. A.

Trustworthiness of the Balance over Long Periods of Time. GEORGE DEAN (T., 1919, **115**, 826—828).

Laboratory Condensers for Use in Reflux Condensation and Distillation Apparatus. O. FAUST (*Zeitsch. angew. Chem.*, 1919, **32**, I, 183—184).—A description is given of condensers, especially suitable for use as reflux condensers, which are provided at the same end with inlet and outlet tubes, one of which passes inside the jacket to the other end of the condenser, whereby counter-current cooling is obtained. The jacket is provided with an air outlet tap. Of the various designs illustrated, one is suitable for connexion in the usual way, another for suspension in the neck of the flask without cork connexion, and a third for fitting bodily into the neck of the distillation vessel.   S. S. A.

Simple Efficient Vacuum Pump for Laboratory Use. ALFRED MAGNUS (*Ber.*, 1919, **52**, [*B*], 1194).—A claim for scientific priority against Volmer (this vol., ii, 225). The application of a current of mercury vapour to the production of high vacua has been utilised by the author (*Inaug. Diss.*, München, 1905).
H. W.

Lecture Experiments [to Illustrate] the Reduction of Hydrogen-ion Concentration. L. GRÜNHUT (*Zeitsch. Elektrochem.*, 1919, **25**, 184—185).—Two experiments are described by which the reduction of the hydrogen-ion concentration may be demonstrated.

(1) By removal of hydrogen ions: 10 c.c. of $0.1N$-hydrochloric acid are placed in each of two 100 c.c. cylinders, and a few drops of a solution of dimethylaminoazobenzene solution added. One cylinder is filled to the mark with distilled water and the other with a $0.1N$-solution of disodium hydrogen citrate. The water solution is red in colour, whilst the other solution becomes yellow. The aqueous solution contains 9·7 mg.-ion per litre ($P_{H^.} = 2.013$), whilst the citrate solution contains 0·015 mg.-ion per litre ($P_{H^.} = 4.83$), that is, the hydrogen-ion concentration has been reduced to 1/650 of its original value. The colour change of dimethylaminoazobenzene occurs between $P_{H^.} = 3$ and $P_{H^.} = 4$.

(2) By repressing the ionisation: 100 c.c. of tartaric acid (40 grams per litre) are placed in each of two 100 c.c. cylinders and coloured blue by the addition of a few drops of methyl-violet solution. To one cylinder, 4 grams of finely powdered sodium tartrate are added; this, when dissolved, will change the colour to violet. The water solution contains 17·00 mg. $H^.$ ion per litre ($P_{H^.} = 1.77$), whilst the tartrate solution contains 0·96 mg. $H^.$ ion per litre ($P_{H^.} = 3.02$). The neutral point of methyl-violet lies between $P_{H^.} = 2$ and $P_{H^.} = 3$.   J. F. S.

Inorganic Chemistry.

Physico-chemical Revision of the Atomic Weight of Bromine: Necessity of Correcting the Atomic Weight of Silver. Pʜ. A. Guʏᴇ (*J. Chim. Phys.*, 1919, **17**, 171—186).— From the experiments of Moles (A., 1916, ii, 42, 526) and Reiman (A., 1917, ii, 137, 200), the weight of the normal litre of hydrogen bromide has been calculated to the value 3·64423 grams. The weight of a litre of hydrogen bromide at 0° and under a pressure of 2/3 or 1/3 atm. is given by 2·42197 grams and 1·20729 grams respectively. The divergences from Avogadro's law $(1+\lambda)$ and from the compressibility (A'_0) have been found to be $(1+\lambda) = 1·00934$ and $A'_0 = 0·00925$ (see this vol., ii, 318). From these values, the atomic weight of bromine is calculated to 79·920. This value is slightly greater than the value obtained from the ratio Ag:Br, consequently it is suggested that the atomic weight of silver ought to be reduced to 107·87.   J. F. S.

Recovery of Iodine from its Residues. F. Aʀɴᴅᴛ (*Ber.*, 1919, **52**, [*B*], 1131—1134).—The residues are placed in a large flask provided with a rubber stopper which carries a tube reaching nearly to the bottom of the liquid. The other end of the tube is connected with a reversed wash-bottle and a source of oxygen. The residues (which should not more than half fill the flask) are acidified with crude sulphuric acid, and oxygen is passed into the flask. A small quantity of nitrite solution is added, the flask is securely corked, and passage of the oxygen is continued into the well-shaken liquid. Completion of the action is indicated by cessation of the oxygen absorption, when a further small quantity of nitrite should be added to make certain that all the iodine has separated. The crude iodine is purified by distillation with steam, the vapours being passed directly into a large Erlenmeyer flask, which is cooled by water and is also provided with a long, upright tube to serve as air condenser. The iodine which is thus obtained retains water with considerable obstinacy, and is most easily dried by warming it on the water-bath in a porcelain dish covered by a clock-glass; the latter is frequently removed and the deposit of moisture and iodine is scraped off. As soon as the sublimate appears perfectly dry, the main portion may safely be regarded as dry also. The iodine so obtained is pure.

If the original solution is free from organic matter of high molecular weight, such as starch, the distillation with steam may be omitted.   H. W.

Electrolytic Production of Fluorine. W. L. Aʀɢᴏ, F. C. Mᴀᴛʜᴇʀs, B. Hᴜᴍɪsᴛᴏɴ, and C. O. Aɴᴅᴇʀsᴏɴ (*J. Physical Chem.*, 1919, **23**, 348—355).—The authors have prepared fluorine by the

electrolysis of molten potassium hydrogen fluoride. The electro-
lysis is effected in an electrically heated copper vessel which serves
as cathode; the anode is made of graphite. The anode is enclosed
in a permeable diaphragm, which prevents the hydrogen liberated
at the cathode mixing with the fluorine. As the electrolysis
proceeds, potassium fluoride and copper fluoride are deposited from
the fusion, and after a while it becomes necessary to regenerate the
electrolyte. The most efficient conditions for work are a tempera-
ture of 240—250° and a current of 10 amperes at 15 volts. Using
these conditions, the current efficiency is about 70%. In the pre-
paration, the potassium acid fluoride must be absolutely dry, and
since this is difficult to obtain and keep on account of the hygro-
scopic properties of the salt, the authors prefer the corresponding
sodium salt, which has the advantages: (i) it is non-deliquescent,
(ii) it decomposes below the fusion temperature, (iii) it contains a
larger quantity of available hydrofluoric acid, and (iv) it is con-
siderably less expensive. The properties of fluorine which may be
used for its detection are: (i) its not unpleasant odour (fluorine
in small quantities is non-toxic, but long exposure to larger quanti-
ties produces headache); (ii) the unlighted gas issuing from a
Bunsen burner is immediately ignited by fluorine; (iii) sulphur and
soft charcoal are quickly ignited when the gas comes into contact
with them.   J. F. S.

Constitution of Sulphur Vapour. JAMES J. DOBBIE and
J. J. FOX (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 484—492).—The
absorption spectrum of sulphur vapour has been photographed at
the temperatures 380—1080°. Sulphur vapour was produced in a
silica tube 100 mm. long and 12 mm. diam., and the measurements
were made with a large Hilger spectrograph. Illumination was
produced by a Nernst lamp for the visible region and the ultra-
violet down to λ 3100, and for the region beyond the range of the
Nernst lamp a cadmium arc was employed. Weighed quantities
of sulphur were vaporised in the tube, which had previously been
sealed at a pressure of 8 mm., the gaseous content being nitrogen;
a further series of experiments was made at atmospheric pressure.
The spectrum shortens as the temperature is raised to 650°, after
which it lengthens again. The maximum absorption therefore
occurs at this point. The authors find on extrapolating the vapour
density results of Biltz (A., 1888, 1027) that at the temperature
650° the density corresponds with a molecule S_3. The authors are
therefore of the opinion that at suitable temperatures sulphur
vapour contains the molecules S_2, S_3, and S_8.   J. F. S.

**The Reduction of Sulphurous Acid by Hydrogen
Sulphide in Aqueous Solution.** ERNST HEINZE (*J. pr. Chem.*,
1919, [ii], **99**, 109—178).—For the quantitative investigation of
the reaction between sulphur dioxide and hydrogen sulphide in
aqueous solution at different temperatures, an apparatus was con-
structed by means of which accurately measured quantities of the

gases could be brought successively into the reaction flask, in which water was already present, with complete exclusion of air. The course of the reaction was found to be very complicated and to involve a number of reversible reactions. It depends both on the relative proportions of the reacting gases used and on the order of addition. A considerable part of the paper is devoted to a description of the special methods devised for the analysis of the reaction liquor. It was found that the sulphur formed in the reaction could be obtained in a readily filterable form if a small quantity of lanthanum chloride was present in the solution. Any remaining hydrogen sulphide was estimated by precipitation with cadmium sulphate; sulphur dioxide was removed by a current of nitrogen, collected in sodium hydroxide solution, and estimated iodometrically, whilst polythionic acids were determined by titrating the remaining solution with barium hydroxide.

It is established, first, that sulphur dioxide enters into the reaction in the form of sulphurous acid, not in the anhydride form. The primary reaction appears to be represented by the reversible equation $H_2SO_3 + H_2S \rightleftharpoons H_2SO_2 + H_2SO$. Precipitation of sulphur is caused by the decomposition of the compound H_2SO, which is assumed to be of the hydrogen peroxide type. This compound is also supposed to be formed by the further action of hydrogen sulphide on the sulphoxylic acid, thus: $H_2SO_2 + H_2S \rightleftharpoons 2H_2SO$. Consequently, the final result of the interaction of one mol. of sulphurous acid with two mols. of hydrogen sulphide is given by the equation $2H_2S + SO_2 = 3S + 2H_2O$. The reaction only comes to completion, however, after several months. The final state is reached more quickly in presence of excess of hydrogen sulphide. It is shown experimentally that hydrogen sulphide also reacts with polythionic acids to form sulphur and water.

When excess of sulphurous acid is present, less sulphur is precipitated and more polythionic acid formed. After about a day, a condition of equilibrium obtains. If, now, the precipitated sulphur is filtered off and the excess of sulphur dioxide removed by a current of nitrogen, in a short time more sulphur comes down and sulphur dioxide again appears in the solution. It is shown that the sulphur, when once precipitated, takes no further part in the process, and the reversible reactions are supposed to involve the polythionic acids, sulphurous acid, and the compounds H_2SO_2 and H_2SO, thus: (4) $H_2SO_2 + SO_2 \rightleftharpoons H_2S_2O_4$;

(5) $H_2SO + H_2SO_3 \rightleftharpoons H_2S_2O_3 + H_2O$;
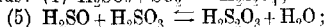
(6) $H_2S_2O_4 + H_2S_2O_3 \rightleftharpoons H_2S_4O_6 + H_2O$; (7) $H_2S_4O_6 + H_2S_2O_3 \rightleftharpoons H_2S_5O_6 + H_2SO_3$. With increasing concentration of sulphur dioxide, the proportion of tetrathionic acid increases, whilst that of pentathionic acid decreases. This is attributed to the dehydration of the sulphurous acid owing to the increasing acidity of the solution, with consequent increase in the production of $H_2S_2O_4$ by equation (4).

When solutions containing excess of sulphur dioxide are allowed to remain for several weeks, increasing quantities of sulphuric acid

are formed, but the mechanism of this change cannot at present be explained. Possibly it is due to the decomposition of trithionic acid, which may be formed in small quantities and is known to decompose into sulphuric acid, sulphur dioxide, and free sulphur.

E. H. R.

Action of Sodium Thiosulphate on the Hypochlorites. F. DIÉNERT and F. WANDENBULCKE (*Compt. rend.*, 1919, **169**, 29—30).—A quantitative study of the interaction of sodium thio-sulphate and sodium hypochlorite in dilute solutions shows that the reaction proceeds according to the equation $3Na_2S_2O_3 + 5Cl_2 + 5H_2O = Na_2SO_4 + 8HCl + H_2SO_4 + Na_2S_4O_6 + 2NaCl$ or $5NaOCl + 3Na_2S_2O_3 + 5H_2O = 2Na_2SO_4 + Na_2S_4O_6 + 5NaCl + 5H_2O$. In the presence of acids, however, or even in the presence of sodium hydrogen carbonate, much less sodium thiosulphate is required, the reaction being $Na_2S_2O_3 + 4Cl_2 + 5H_2O = 2NaHSO_4 + 8HCl$.

W. G.

Selenic Acid and Copper Selenate. L. M. DENNIS and J. P. KOLLER (*J. Amer. Chem. Soc.*, 1919, **41**, 949—970).— Selenium has been obtained from smelter flue-dust by fusing a mix-ture of 300 grams of flue-dust, 200 grams of anhydrous sodium carbonate, and 775 grams of sodium peroxide in a large nickel crucible until the mass melted quietly. After cooling, the product was treated with water and insoluble material filtered off; it was then nearly neutralised with hydrochloric acid, which precipitated most of the zinc and aluminium. After filtration, a large volume of hydrochloric acid was added, and the solution boiled for thirty minutes to reduce selenic acid to selenious acid; any silica present was precipitated at this stage; the filtrate was then heated to 80° and treated with sodium sulphite in small quantities. The selenium separates, and is converted into the grey modification by digesting it with the solution for several hours at 80°.

Anode slimes containing 96% of selenium were also used to pre-pare the pure element. The slime was added to concentrated nitric acid to which one-fifth of its volume of water had been added; a vigorous action ensued, and when this had moderated, the mixture was heated to complete the oxidation. The solution was filtered, and a viscous, dark green liquid obtained which was evaporated to dryness. The residue was taken up with hydrochloric acid (3:1) and the selenium precipitated by sulphur dioxide or sodium sulphite.

Pure selenium dioxide is prepared from selenium by dissolving the substance obtained above in nitric acid and evaporating the solution to dryness. The crude dioxide thus obtained was placed in one end of a glass tube 85 cm. long and 3·5 cm. diameter. The tube was covered with asbestos paper and placed in a 60 cm. com-bustion furnace; a 2 cm. thick plug of glass wool was placed in the middle of the tube. The tube was so arranged in the furnace that

only a small length protruded at the cold end. On heating the crude dioxide, it sublimed and condensed on the protruding part of the tube, and as this became full, more of the tube was pushed out of the furnace.

Selenious acid was prepared directly from anode slimes by oxidising with nitric acid and evaporating until a syrupy solution was obtained. On cooling, large crystals separated, and after four recrystallisations from water, pure selenious acid, quite free from tellurium, was obtained.

Tellurium may be detected in the presence of selenium by dissolving 10—20 grams of the oxide in hydrochloric acid (D 1·16), heating to 90°, and saturating with sulphur dioxide. The precipitated selenium is filtered off and the filtrate diluted with an equal volume of water and saturated cold with sulphur dioxide. An immediate black precipitate of tellurium is formed if this element is present. A yield of 1200 grams of selenious acid was obtained from 3000 grams of slimes.

Pure selenic acid has been prepared (i) by the oxidation of silver selenite by means of bromine, (ii) by the oxidation of copper selenite by chlorine, and (iii) by the electrolytic oxidation of selenious acid. In the last-named method, the most efficient yield is obtained when lead dioxide anodes, in thimbles, are used.

Selenious acid may be detected in the presence of selenic acid on the basis of the reaction $H_2SeO_3 + 4HI = Se + 4I + 3H_2O$. Concentrated seleric acid will also oxidise hydriodic acid, but if the solution is dilute, selenic acid will remain unchanged. If, therefore, small quantities of potassium iodide are added to solutions containing both selenious and selenic acid in test-tubes 15 cm. long, there will be a yellow colour produced, due to iodine being liberated, and when the colour of the iodine is discharged by the addition of a drop or two of sodium sulphite, the red turbidity due to free selenium is visible. If the selenic acid is more concentrated than 0·8%, iodine may be liberated by it, but as the hydriodic acid is not concentrated, the reaction goes no further. This reaction is capable of detecting 1 part of selenium dioxide in 18,400 parts of selenic acid, or 1 part of selenium dioxide in 2,500,000 parts of solution.

Sulphuric acid in the presence of selenic acid may be detected in the following manner. Selenic acid is diluted to 4%, placed in a 350 c.c. beaker, 10 c.c. of 90% hydrazine hydrate added, and heated to 60°. Sufficient concentrated hydrochloric acid (5 c.c.) is added to make the liquid distinctly acid, and the mixture boiled for an hour. After cooling, the precipitated selenium is filtered off, and the process repeated until no more selenium is deposited. The filtrate is then evaporated to 25 c.c., and 2 c.c. of 10% barium chloride solution are added, and the mixture kept at 80° for an hour, when a white turbidity is produced if sulphuric acid is present. This reaction is visible if 1 mg. of barium sulphate is formed, and it is possible to detect 1 part of sulphuric acid in the presence of 10,000 parts of selenic acid.

All attempts to prepare perselenic acid and perselenates by electrolysis gave negative results.

The monohydrate of copper selenate is produced from the pentahydrate by heating the latter at 102° for two hours. The pentahydrate is completely dehydrated at 230—235°, and the anhydrous selenate is stable up to 280°. The pentahydrate used in these experiments was prepared by the action of chlorine on copper selenite, and contained copper chloride; this was removed by extracting with acetone in a Soxhlet extractor. In this process, the pentahydrate lost 2H$_2$O and the trihydrate was formed; this substance has a pale blue colour.

Ammonia derivatives of copper selenate have been prepared by methods analogous to those used by Horn and Taylor (A., 1904, ii, 662) in the preparation of the corresponding derivatives of copper sulphate. (i) *Copper selenate tetra-ammoniate monohydrate*, CuSeO$_4$,4NH$_3$,H$_2$O, is prepared by digesting 100 grams of copper selenate pentahydrate with 125 c.c. of ammonium hydroxide (0·96) until it has dissolved; ammonia gas is then led in, and in a short time clusters of deep bluish-violet crystals separate. The crystals were dried by suction and finally air-dried. It is quite stable when kept over lime, but loses ammonia in the air; it crystallises in slender, orthorhombic prisms. (ii) *Copper selenate triammoniate monohydrate*, CuSeO$_4$,3NH$_3$,H$_2$O, is prepared by exposing the last described compound to a current of air for about twenty-four hours. It is a blue compound which dissolves in water to give a blue solution;' this on dilution becomes lighter in colour and deposits a basic salt. (iii) *Copper selenate tetra-ammoniate*, CuSeO$_4$,4NH$_3$, is prepared from the first-named compound by placing it moist in a desiccator over lime at 25 mm. pressure and keeping it there for seven days. It is of a lighter bluish-violet colour than the hydrated salt; it gives off ammonia when exposed to the air, but is stable in a vacuum over lime.

J. F. S.

Formation of Ammonia by Means of an Electric Arc: Influence of Diminishing the Pressure. E. BRINER and A. BAERFUSS (*J. Chim. Phys.*, 1919, **17**, 71—140. Compare this vol., ii, 148).—The synthesis of ammonia from a mixture of nitrogen and hydrogen at reduced pressures by means of an alternating arc between electrodes of various metals has been studied under a long series of widely varying experimental conditions. It is shown that at sufficiently low pressures (150 mm. and below) the arc assumes the appearance of a luminous sheath, which surrounds the electrodes and becomes longer the lower the pressure and the larger the current. This sheath plays an important part in the synthesis of ammonia. On reducing the pressure, it is noted that successive decreases in the voltage of the arc have nearly the same effect in the two pure gases and their mixtures. At pressures of the order 600—700 mm., an increase in the arc current leads to an increase in the energy yield (Rdt), which is due to a lowering of the

voltage. Working at pressures of the order 100 mm. with the theoretical mixture of gases, there is an improvement in the value of Rdt which is to be attributed, for the most part, to the lowering of the voltage. At this pressure and with platinum electrodes, an increase in the nitrogen percentage leads to an increased quantity yield (Q) of about 200% for the optimum mixture of five volumes of nitrogen to one volume of hydrogen. Using different metals as electrodes, it is found that the metals of the platinum group give the best results, platinum itself being most efficient; these metals are followed in efficiency by tungsten and copper. Iron and nickel are very much less effective than the other metals mentioned, and for these the optimum yield is obtained from the theoretical mixture at all pressures. The presence of moisture does not appear to affect the synthesis; the presence of oxygen in small quantities in certain circumstances acts favourably on the reaction. At reduced pressures, the influence of the arc current appears to be connected with the temperature produced at the electrodes; for every electrode there is an optimum diameter for every current. For currents up to 0·020 amp., cooling of the region containing the arc does not increase the yield. At low pressures, the yields are almost independent of the distance between the electrodes, consequently it is advisable to reduce this space as much as possible, since it only plays a secondary part in the reaction. There is no appreciable formation of ammonia when nitrogen and hydrogen, which have been submitted to the arc, are allowed to mix. The foregoing results confirm in the main the theory of the formation of ammonia put forward by the authors. This theory states that ammonia is formed by the action of a high temperature followed by a kinetic phenomenon in the colder regions where the ammonia is stable in the concentration produced, rather than by the establishment of an equilibrium in the very cold regions. In the relatively cold regions, which are near the luminous sheath, the formation occurs between the elements which have previously been rendered active by contact with the electrodes. The activation of the elements appears to consist of the dissociation of the molecules into atoms at the very high temperature of the arc, and is favoured by a diminution of the pressure. Active nitrogen, described by Strutt, does not appear to take any part in the synthesis, and at the pressures employed does not appear to be formed.   J. F. S.

Relations between Nitrogen Peroxide and Nitric Acid.
PASCAL and GARNIER (*Bull. Soc. chim.*, 1919, [iv], **25**, 309—321).
Results obtained for the density of nitrogen peroxide over the temperature range 0—21·5° are in agreement with those of Tyndall (compare T., 1891, **59**, 1076), being represented by the equation $D_4^t = 1·490 - 0·00215t$. The density of nitrogen peroxide is varied by the addition of nitrous anhydride, the variations of density with the composition of the mixture obeying a linear law. The density of nitric acid shows a marked increase with the addition of nitrogen peroxide (compare Lunge and Marchlewsky,

Zeitsch. angew. Chem., 1912, 10), reaching a maximum when the mixture contains about 42·5% by weight of the peroxide. This corresponds with a hydrate, N_2O_5,N_2O_4,H_2O, and the existence of this is confirmed by a thermal study of the reciprocal solubilities of nitric acid and nitrogen peroxide. This hydrate is stable below $-48·5°$, and at this temperature dissociates, liberating nitrogen peroxide.

Sulphuric acid is not appreciably soluble in nitrogen peroxide, but when added to anhydrous nitric acid or the acid containing a little water, it does not appreciably alter the solubility of the peroxide in the acid providing the mixture does not contain more than 30% of sulphuric acid, the water content being the principal factor of solubility.

W. G.

Some Properties of Acid Phosphates. A. JOANNIS (*Compt. rend.*, 1919, **168**, 1202—1203).—Neither disodium hydrogen phosphate nor potassium dihydrogen phosphate absorbs gaseous or liquid ammonia, and ammonium dihydrogen phosphate only absorbs it very slowly. Similarly, in the absence of water, magnesium ammonium phosphate cannot be obtained from magnesium hydrogen phosphate.   W. G.

Allotropy of Carbon. MAURICE COPISAROW (*Chem. News*, 1919, **118**, 301—304).—The polyatomicity of the carbon molecule is proved by (i) the existence of several forms of carbon which are chemically and physically distinct from one another, (ii) the high volatilisation point, (iii) the general theory of the solid state, (iv) the products of moist oxidation, (v) the combustion of carbon, and (vi) the X-ray spectrometric study of the modifications of carbon. In accordance with the theory of allotropy (this vol., ii, 279), carbon may exist in three forms: (a) a non-rigid, molecular configuration, some valencies of which are free, (b) a rigid, molecular configuration, some valencies of which are free, and (c) a rigid, molecular configuration, all valencies of which are fixed. From a consideration of the heats of combustion, products of oxidation, and the physical properties of the three forms of carbon, it is shown that amorphous carbon is represented by a, graphite by b, and diamond by c. Possible configurations in keeping with the above are drawn in the paper.   J. F. S.

The Oxidation of Coal. FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER (T., 1919, **115**, 895—902).

The Preparation of Carbonyl Chloride by Means of Carbon Tetrachloride and Oleum or Ordinary Sulphuric Acid. V. GRIGNARD and ED. URBAIN (*Compt. rend.*, 1919, **169**, 17—20).—With sulphur trioxide, carbon tetrachloride reacts according to the equation $2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2$, but with pyrosulphuric acid the reaction is $SO_3 + H_2SO_4 + CCl_4 = COCl_2 + 2SO_3HCl$. With ordinary sulphuric acid in the presence of

infusorial earth as a catalyst, the reaction is $2H_2SO_4 + 3CCl_4 = 3COCl_2 + 4HCl + S_2O_5Cl_2$, together with a slight secondary reaction, $S_2O_5Cl_2 + CCl_4 = COCl_2 + 2SO_2Cl_2$. The principal objection to this second method is the presence of hydrogen chloride with the carbonyl chloride, but this may be got over to some extent by dissolving the carbonyl chloride in carbon tetrachloride, the hydrogen chloride being only slightly soluble in this solvent. [See, further, *J. Soc. Chem. Ind.*, 1919, August.]

W. G.

Action of Concentrated Sulphuric Acid on Carbon Tetrachloride. CH. MAUGUIN and L. J. SIMON (*Compt. rend.*, 1919, **169**, 34—36. Compare Grignard and Urbain, preceding abstract).—Real sulphuric acid reacts with carbon tetrachloride at about 150° according to the equation $CCl_4 + H_2SO_4 = SO_3HCl + COCl_2 + HCl$. If an acid which is slightly aqueous is used, the water present is decomposed by the chlorosulphonic acid first formed, giving sulphuric acid and hydrogen chloride. Finally, the chlorosulphonic acid itself reacts with carbon tetrachloride, thus: $CCl_4 + 2SO_3HCl = S_2O_5Cl_2 + 2HCl + COCl_2$. The carbonyl chloride is purified by solution in carbon tetrachloride and subsequent distillation.

W. G.

The Sulphones formed by the Iodides of Sodium, Rubidium, and Cæsium. R. DE FORCRAND and F. TABOURY (*Compt. rend.*, 1919, **168**, 1253—1257).—By the action of liquid sulphur dioxide on the iodides of sodium, rubidium, and cæsium, the authors have obtained sulphones of the type $MI,3SO_2$, that of sodium being amorphous and the other two being soluble in excess of liquid sulphur dioxide, and crystallising from it on evaporation at 0°.

W. G.

Stability of Sodium Thiosulphate Solutions. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 878—888).—In general, the decomposition of thiosulphate solutions proceeds more rapidly in the light than in the dark. The oxidising action of the air may be prevented to some extent by covering the solution with a layer of light petroleum. The presence of alkaline substances prevents the decomposition almost completely. The addition of about 0·2 gram of sodium carbonate per litre is sufficient to ensure in great measure the stability of the solution. The accelerative effect of deposited sulphur on the decomposition is probably due to bacterial action. The decomposition may be retarded by the addition of 0·01 gram of mercuric iodide per litre of solution.

W. S. M.

Sodium Hydrogen Sulphite Crystals $(NaHSO_3,3H_2O)$.— WALTHER SCHÜLER and ARNO WILHELM (*Zeitsch. angew. Chem.*, 1919, **32**, 198—199).—The sodium hydrogen sulphite crystals deposited at low winter temperatures from aqueous solutions contain three molecules of water. They are 2—6 cm. long, 2—3 mm.

thick, hexagonal in section, and belong apparently to the rhombic system. At higher temperatures or when removed from the mother liquor, they rapidly lose water and disintegrate, leaving a residue of anhydrous sodium hydrogen sulphite containing sulphate and traces of pyrosulphite if they have been exposed to the air.

G. F. M.

Lime Mortars : Solution and Conversion of Solid Substances into Colloids. V. KOHLSCHÜTTER and G. WALTHER (*Zeitsch. Elektrochem.*, 1919, **25**, 159—183).—The rate at which calcium oxide, prepared from calcium carbonate, calcium hydroxide, and calcium oxalate, respectively, combines with water vapour at the ordinary temperature has been determined. The volume changes and the amount of water taken up have also been determined. The rate of absorption is shown to differ with the various samples of calcium oxide. Further, the rate of sedimentation of calcium hydroxide has been measured for calcium hydroxide prepared by slaking lime in water or solutions of calcium chloride, calcium nitrate, sodium chloride, potassium chloride, potassium nitrate, sodium hydroxide, sodium acetate, potassium thiocyanate, ammonia, ammonium oxalate, and sodium carbonate of various concentrations. The rate at which sedimentation occurs varies with the different electrolytes; some when in small concentrations increase the sedimentation velocity, and in large concentrations decrease it, whilst in other cases the reverse is the case. The velocity of sedimentation is greater when water is added to quicklime than when lime is added to water. Further, a difference is observed in the rate of sedimentation of calcium hydroxide produced by slaking lime in lime-water. The sedimented product of a suspension of calcium hydroxide in water is not the same as the product obtained by slaking lime in water and allowing it to settle. The results obtained indicate that in the production of a true solution of calcium hydroxide in water from lime, an intermediate colloidal state is first formed.   J. F. S.

Lead–Sodium–Mercury and Lead–Sodium–Tin Alloys. J. GOEBEL (*Zeitsch. anorg. Chem.*, 1919, **106**, 209—228).—A thermal investigation has been made of lead–sodium–mercury alloys containing up to 4% of sodium and 7% of mercury, and of lead–sodium-tin alloys containing up to 4% of sodium and 6% of tin. The lead–sodium binary alloys show a eutectic point at 308° with 2·7% of sodium, the eutectic consisting of mixed crystals of sodium and lead with a compound, probably Na_2Pb_5, which corresponds with 4% of sodium. To obtain the equilibrium diagram of the lead–sodium–mercury alloys, sixty-three fusions were made. In presence of mercury up to 2%, the lead–sodium eutectic persists, but the eutectic point is lowered about 5°. With more mercury, up to 7%, the eutectic point disappears, but is still represented in the diagram by a minimum in the same position. Sodium is more soluble in the lead–mercury mixed crystals than in pure lead. A

plan of the space diagram with isothermal lines is given. The series of fusions with 3% of mercury was extended up to 12% of sodium. The liquidus line rises from 2·7% to about 5% of sodium, then falls to a eutectic point between 7 and 8% of sodium at 290°, and again rises to a high maximum at 354° with 10% of sodium. It then falls rapidly towards another eutectic line at 280°. The existence of at least two compounds is indicated, but their nature is not apparent.

To obtain the equilibrium diagram for the lead–sodium–tin system up to 4% of sodium and 6% of tin, forty-eight fusions were made. The space diagram consists of two surfaces meeting in a depression running parallel to the lead–tin side of the diagram. This depression represents the separation of a eutectic consisting of lead–sodium mixed crystals with an unknown compound. The temperature of the eutectic point falls with increasing quantities of tin from 308° to 296°. The lead–tin mixed crystals appear to dissolve no more sodium than pure lead.   E. H. R.

Reduction of Metallic Sulphides by Means of Aluminium.

N. PARRAVANO and P. AGOSTINI (*Gazzetta*, 1919, **49**, i, 103—115. Compare Parravano and De Cesaris, A., 1917, ii, 292).—The displacement of the metal of a sulphide by another metal in accordance with the equation $M^1 + MS \rightleftharpoons M^1S + M$ is considered in the two cases: (1) when the reacting compounds are able to exist together without mixing, and (2) when such compounds are more or less miscible in the liquid state alone or in both the liquid and solid states.

In the experiments made, the metallic sulphide was added to molten aluminium contained in a clay crucible, the reacting substances being taken in weighed quantities. The fused mass was then gradually heated and stirred until reaction commenced, and after a short time was allowed to cool. In all cases, the apparatus was surrounded by an inert gas.

The sulphides investigated were PbS, Cu_2S, SnS, CdS, ZnS, Sb_2S_3, Ag_2S, Bi_2S_3, NiS, and CoS, all of which were largely, and some completely, desulphurised by aluminium. Noteworthy is the reduction of zinc sulphide, to which is attributed a higher heat of formation than to the equivalent proportion of aluminium sulphide. With PbS, Cu_2S, SnS, Ag_2S, and Bi_2S_3, the amount of the metal obtained approximates closely to the theoretical quantity, whereas this is not the case either (1) with CdS and ZnS, owing to the volatility of the reduced metal, or (2) with NiS and CoS, owing to projection of material from the crucible in consequence of the excessive vigour of the reaction.   T. H. P.

New Synthesis of Phosgenite.

W. A. HAMOR and H. E. JILL (*Amer. J. Sci.*, 1919, [iv], **47**, 430).—Phosgenite, $PbCO_3,PbCl_2$, has been synthesised by heating a mixture of lead hydroxide and excess of carbonyl chloride for one to four hours at 55°, 120°, 150°, 175°, 200°, and 250°. The best results were

obtained at 175°, the amount formed being less the higher the temperature above this value. The product was crystalline and of a faint yellow colour, identical in all respects with the naturally occurring mineral.   J. F. S.

Combinations of Mercuric Chloride and the Alkali Chlorides. C. TOURNEUX (Ann. Chim., 1919, [ix], 11, 225—361). —From a study of the equilibrium of the system mercuric chloride-potassium chloride–water at 34°, 56°, 80°, and 100°, the author shows that it is possible to obtain two crystalline salts having the composition $HgCl_2,2KCl,H_2O$ and $2HgCl_2,KCl,2H_2O$. In addition, three sets of crystals have been obtained, the composition of which may be represented by $(2HgCl_2,KCl,H_2O)_4(HgCl_2,2KCl,H_2O)$, $(2HgCl_2,KCl,H_2O)(HgCl_2,2KCl,H_2O)$, and $(2HgCl_2,KCl,H_2O)(HgCl_2,2KCl,H_2O)_4$.

The author is not certain as to whether the last three formulæ represent double salts or simply mixed crystals of the two salts the composition of which is expressed in the brackets. He has not succeeded in preparing the hydrate $2HgCl_2,KCl,H_2O$. He has verified the existence at the ordinary temperature of the following crystalline salts: $HgCl_2,RbCl,H_2O$; $HgCl_2,NaCl,2H_2O$; $HgCl_2,NH_4Cl,H_2O$; $4HgCl_2,3RbCl,H_2O$.

The crystalline double salts formed by mercuric chloride and the alkali chlorides are all homœomorphic and show a marked chemical analogy. The analogy of the properties of these crystals with those of the zeolites suggest that the water content of the crystals depends on the vapour tension of the surrounding medium.
                                                                    W. G.

Extraction of Gallium and Germanium from Zinc Oxide. H. C. FOGG and C. JAMES (J. Amer. Chem. Soc., 1919, 41, 947—949).—Some zinc ores contain small, though appreciable, amounts of germanium and gallium, and, these metals being less volatile than zinc, remain behind in the retorts when the zinc distils off. These residues furnish a good source for the elements; gallium and germanium, although the amounts obtainable vary enormously; for example, 100 lb. of one specimen gave 8 grams of pure gallium, whilst a second sample of 200 lb. yielded only the merest traces; the amount of germanium in the two samples was almost identical. One kilo. of the oxide prepared from the zinc residues was treated with 2400 c.c. of commercial hydrochloric acid in a large flask, the oxide being added in small portions to the acid to prevent caking. When all had dissolved, a little potassium chlorate was added carefully until, after vigorous shaking, oxides of chlorine were evolved. The flask was then connected to a condenser and a thermometer placed with its bulb in the liquid, and the liquid distilled; two fractions were collected, the first, up to 121°, containing very little germanium, and the second, up to 135—140°, containing practically the whole of the

germanium.   The distillates from several quantities were then saturated with hydrogen sulphide, and the white sulphide filtered off.   The liquid left in the flask was diluted with a litre of water and lead chloride allowed to settle.   The clear liquid was decanted from the sediment and treated with ammonium hydroxide until a slight permanent precipitate was formed, metallic zinc was added, and the whole digested at the boiling point for several hours.   The precipitation was considered complete when a portion of the super-natant liquid gave a precipitate of basic zinc chloride on dilution with water.   The precipitated metals and basic salts were filtered off and the filtrate examined spectroscopically to ascertain if all the gallium had been precipitated.   Ten such precipitates, corre-sponding with 30 kilos. of the original oxide, were united, dis-solved in commercial hydrochloric acid with the aid of a little potassium chlorate, boiled, and lead chloride allowed to separate. This was removed and the solution saturated with hydrogen sulphide.   The precipitate was filtered off and the filtrate boiled, neutralised with dilute ammonium hydroxide until a permanent precipitate just formed, and again digested with zinc at the boil-ing point.   When the solution had turned basic, it was poured from the precipitate, diluted, and filtered, the operation being repeated with the filtrate until the basic precipitate ceased to show a gallium spectrum.   The precipitates poor in gallium were placed with those first obtained from the crude zinc chloride.   The pre-cipitates rich in gallium were again dissolved in hydrochloric acid, the solution nearly neutralised, saturated with hydrogen sulphide, and filtered.   The filtrate was treated with ammonium chloride, made alkaline to litmus with ammonia, and boiled until just acid. A gelatinous precipitate consisting of gallium, aluminium, and iron hydroxides was filtered off and washed.   From 100 lb. of the crude zinc oxide, 60 grams of the mixture of hydroxides was obtained. These were dissolved in the minimum quantity of hydrochloric acid, diluted with water, and nearly neutralised with sodium hydroxide. After the addition of a little formic acid, the liquid was treated with an excess of sodium formate, the precipitate collected, and thoroughly washed to ensure the complete removal of zinc.   The precipitate and filter paper were placed in water in a casserole, saturated with hydrogen sulphide, and digested with cold 1% hydro-chloric acid.   The insoluble tin and cadmium sulphides were removed by filtration.   The filtrate was made slightly alkaline with ammonia, boiled until slightly acid, and the gallium and aluminium hydroxides filtered off.   These were dissolved in the minimum quantity of hydrochloric acid, and an excess of sodium hydroxide solution added.   The solution was then electrolysed by a current of 1·5 amperes, using platinum electrodes 3 cm. sq.   The gallium was deposited on the cathode in bright, shining globules, which dropped off as they became larger.   When no more gallium was deposited, the solution was poured off and the metal washed several times with water, and the globules then united by the addition of a few drops of concentrated hydrochloric acid.   J. F. S.

Monoclinic Double Selenates of the Iron Group. A. E. H. TUTTON (*Phil. Trans.*, 1919, [*A*], **218**, 395—440).—The crystallographic and optical investigation of the crystals of the four salts of the series $R_2M(SeO_4)_2,6H_2O$, in which M is ferrous iron and R is potassium, rubidium, cæsium, and ammonium, has been completed, and the detailed results are recorded in this paper. The examination of the crystals of the potassium salt was accomplished under great difficulties on account of the rapid decomposition of the crystals, apparently into the dihydrate, at temperatures very little above 0°. Suitable crystals were obtained on four very cold nights, and the necessary measurements were made by intensive working in a room the temperature of which never exceeded 6°.

The salts all crystallise in the holohedral class of the monoclinic system, and are closely isomorphous with the other salts of this extensive series. In this group, as in other groups of the series, there is a regular progression in the habit and dimensions of the crystals from the potassium, through the rubidium, to the cæsium salt, whilst the ammonium salt approximates closely in most respects to the rubidium salt.

Potassium ferrous selenate, $K_2Fe(SeO_4)_2,6H_2O$, $a:b:c=0.7490$: $1:0.5044$, $\beta=103°50'$, D_4^{20} 2·494, M.V. 210·39.

Rubidium ferrous selenate, $Rb_2Fe(SeO_4)_2,6H_2O$, $a:b:c=0.7424$· $1:0.5000$, $\beta=104°57'$, D_4^{20} 2·800, M.V. 220·29.

Cæsium ferrous selenate, $Cs_2Fe(SeO_4)_2,6H_2O$, $a:b:c=0.7308:1$: 0.4979, $\beta=106°2'$, D_4^{20} 3·048, M.V. 233·21.

Ammonium ferrous selenate, $(NH_4)_2Fe(SeO_4)_2,6H_2O$, $a:b:c=$ $0.7433:1:0.5019$, $\beta=106°9'$, D_4^{20} 2·191, M.V. 220·39.

The regular, progressive change in the dimensions of the crystal structure in the isomorphous series on passing from potassium to cæsium is associated with the regular increase in the atomic number of the alkali metal. The isomorphism of the ammonium salts with those of the alkali metals is held to be proof of the invalidity of the Barlow-Pope theory of valency volume.   E. H. R.

Triboluminescence of Uranium Compounds. J. A. SIEMSSEN (*Chem. Zeit.*, 1919, **43**, 267).—The author has made experiments with a number of samples of uranium nitrate in an attempt to obtain explosive crystals of the kind reported by Ivanov (A., 1912, ii, 455) and Andrews (A., 1913, ii, 60). In no cases were explosive crystals obtained, but generally they showed the property of triboluminescence. It is concluded that the explosive crystals observed by the above authors owed their property to the presence of a labile nitric oxide compound. The triboluminescence of uranium salts is attributed to electrical tension in the crystals.   E. H. R.

Analytical Chemistry.

The Use of Freezing-point Determinations in Quantitative Analysis. CHARLES EDWARD FAWSITT (T., 1919, **115**, 801—808).

Calculation of Possible Error in Volumetric Analysis. V. ZOTIER (*Bull. Sci. Pharmacol.*, 1918, **25**, 274—282, 357—364; from *Chem. Zentr.*, 1919, ii, 636—639).—A mathematical paper in which the inaccuracies inherent in volumetric analysis are considered. The errors arise from incorrect calibration and reading errors in measuring vessels (pipette and burette) and from uncertainty with respect to the end-point of the indicator. The various methods of preparing standard solutions are also treated, as well as errors due to impurity in the standard substance. A mathematical expression taking these factors into account is derived, for details of which the original must be consulted. It is thus calculated that the possible error in the determination of chlorine in commercial salt (1 gram of substance dissolved in 100 c.c. and titration of 20 c.c. of the solution with $N/10$-$AgNO_3$) is about 1 in 100.   H. W.

New and Rapid Apparatus for Electrochemical Analyses. J. T. KING (*Chem. and Met. Eng.*, 1919, **21**, 25—29).—In electrochemical analyses, agitation of the electrolyte hastens deposition of the metal, and the author has originated a more efficient method of agitation by rotating the containing beaker. Two experimental designs and the final form of apparatus are described. Besides the method of stirring, the system of wiring and the electrode holders are novel. The circuit is not broken when a beaker is lowered and a cell removed from the circuit. The operation of the apparatus and the method of carrying out an analysis are described. Tests were made on copper solutions of known strength to determine the speed and accuracy of the apparatus, and the results are tabulated. With currents of three, six, and nine amperes, the times taken to deposit 1 gram of copper were found to be thirty-five, twenty-five, and sixteen minutes respectively. Three unknown brasses were analysed for copper, and the results obtained by this and other methods of stirring, and carried out by different operators, are tabulated, and show excellent agreement.   T. H. B.

Comparative Tests of "Palau" and "Rhotanium" Ware as Substitutes for Platinum Laboratory Utensils. L. J. GUREVICH and E. WICHERS (*J. Ind. Eng. Chem.*, 1919, **11**, 570—573).—"Rhotanium A" ware (gold, 90%; palladium, 10%) is superior to platinum as regards resistance to loss on heating, boiling hydrochloric and hydrofluoric acids, boiling 20% sodium hydr-

oxide solution, sulphuric acid, and fusion with sodium carbonate or potassium pyrosulphate, but inferior as regards the action of nitric acid, ferric chloride solution, and fused sodium hydroxide. It must not be heated higher than 1100°. "Rhotanium C" (gold, 70%; palladium, 30%) and "palau" (gold, 80%; palladium, 20%) alloys are superior to platinum as regards heating up to 1200°; they behave towards reagents similarly to "rhotanium A," but are not suitable for potassium pyrosulphate and sodium hydroxide fusions.   W. P. S.

Sulphite Leuco-derivatives of Triaminotriphenylmethane as Reagents for Alkalinity and for Dissociation of Salts.

I. GUARESCHI (*Gazzetta*, 1919, **49**, i, 115—123).—Magenta and other colouring matters of the triphenylmethane group, when reduced by means of sulphur dioxide or a hydrogen sulphite, serve as good reagents for bromine and hypobromites (A., 1912, ii, 989), and it is now found that they are also applicable to the detection of alkalinity, particularly with potable waters. The constitution of these compounds still remains undecided (compare Hantzsch and Ostwald, A., 1900, i, 256). The sensitiveness of the reaction is such that preliminary concentration of the water by evaporation is unnecessary; the intensity of the coloration is greater when an ethyl group than when a methyl group is present in the leuco-derivative, and still greater when the ethyl group is united to an imino-group.

Decolorised triethylrosaniline hydrochloride (Hofmann's violet) gives an intense violet coloration with dilute solutions of faintly alkaline salts, such as calcium hydroxide, carbonate or hydrogen carbonate, dimetallic hydrogen phosphates, borates, lead salts (normal or basic acetate), sodium acetate, basic quinine sulphate, aniline, magnesium phosphate, and magnesium ammonium phosphate; the reaction is more sensitive than that with litmus or other indicator. Wheat starch, which contains no proteins, gives no coloration, whereas rice starch, always containing more or less protein matter, reacts distinctly. The colouring matter formed is highly adherent to glass. With distilled water, or with dilute solutions of neutral salts like sodium chloride, no reaction takes place within an hour, and only a very faint coloration appears after a long time.

Similar colorations are given by magenta, *p*-rosaniline hydrochloride, methyl-violet, and crystal-violet, previously decolorised by sulphur dioxide. The coloration of the crystal-violet reagent by hypochlorites (compare Le Roy, A., 1916, ii, 535) is given also by solutions having an alkaline reaction, but free from hypochlorite.
                                                          T. H. P.

Estimation of Perchlorates, Alone, or in the Presence of Chlorates and Chlorides.   J. GUILFOYLE WILLIAMS (*Chem News*, 1919, **119**, 8).—Perchlorates, but not chlorates, are reduced by titanium trichloride solution in hot acid solution. At

excess of titanium trichloride is used, and this excess is subsequently titrated with ferric sulphate solution. [See, further, *J. Soc. Chem. Ind.*, 1919, August.]   W. P. S.

Estimation of Iodide in Mineral Waters and Brines.

W. F. BAUGHMAN and W. W. SKINNER (*J. Ind. Eng. Chem.*, 1919, **11**, 563—568).—A quantity of the sample containing not more than 0·1 gram of iodine or more than 10 grams of total salts is diluted to 100 c.c., boiled with the addition of sodium hydroxide and sodium carbonate, and filtered. The filtrate is neutralised with sulphuric acid, 1 c.c. of 4% sodium hydroxide solution is added, the mixture boiled, an excess of potassium permanganate is added, and this excess then decomposed by treating the cold mixture with alcohol. After filtration, the solution is treated with 2 grams of potassium iodide, acidified with hydrochloric acid, and the liberated iodine titrated with thiosulphate solution. If it is desired to estimate bromine in the sample, the iodine may be first separated by steam distillation with the addition of ferric sulphate; the distilled iodine is collected in potassium iodide solution and titrated.   W. P. S.

A Modified "Etching" Test for Fluorides. WILLIAM

PARTRIDGE (*Analyst*, 1919, **44**, 234—235).—The substance under examination is treated with 2 or 3 c.c. of 25% (by volume) sulphuric acid, the liquid covered with a layer of butter fat, and the test-tube placed upright in water at 80° to 95° for three hours. In the presence of 0·01 gram of sodium fluoride, the glass in contact with the acid will be "etched," and the markings will not be affected by successive treatment with ether, boiling alcohol, and boiling hydrochloric acid, or by rubbing with a piece of wood.   C. A. M.

Method of Analysis of Fluospar and of Basic Slags containing Fluorine. G. R. DOYLE (*Chem. News*, 1919, **118**,

304—305).—Half a gram of the finely powdered sample is weighed into a dish, converted into a paste with 5 c.c. of water, and evaporated on a water-bath almost to dryness with 35 c.c. of glacial acetic acid. A further quantity of 25 c.c. of glacial acetic acid is added, and the mass evaporated to dryness on a water-bath and then heated in a steam-oven until all acid has been expelled. The residue is transferred to a beaker and diluted to 80 c.c., boiled, and filtered. The filtrate contains (*a*) available lime (CaO or $CaCO_3$), (*b*) soluble silica, (*c*) manganese, (*d*) magnesia, (*e*) lead, whilst the residue contains (*a*) all calcium existing as CaF_2, (*b*) silica, and (*c*) iron and alumina. The residue is ignited in a platinum dish, cooled, weighed, treated with hydrofluoric acid, evaporated to dryness, ignited, and weighed. The loss in weight gives the amount of silica present. The remaining residue is treated with 5 c.c. of sulphuric acid and evaporated until fumes are evolved, then it is ignited and weighed. The gain in weight is the increase of calcium sulphate over calcium fluoride, $CaSO_4 \times 0·5735 = CaF_2$. The residue is boiled for twenty minutes

with 20 c.c. of hydrochloric acid, diluted, and precipitated by the addition of ammonium chloride and ammonia, boiled, filtered, ignited, and weighed. The weight is deducted from the weight of iron, aluminium, and calcium fluoride, and gives the weight of calcium fluoride. If lead is present, it must be removed by hydrogen sulphide before the iron and aluminium are precipitated. The filtrate is estimated in the usual way.   J. F. S.

Estimation of the Oxygen Content of Organic Substances.

ROBERT STREBINGER (*Zeitsch. anal. Chem.*, 1919, **58**, 97—114).— Oxidation by heating at 200° with a mixture of potassium iodate and sulphuric acid, and subsequent iodometric titration of the excess of iodate, affords a means of estimating the oxygen content of organic substances provided that the percentage amounts of the other constituents are known. The method is applicable to substances containing carbon, hydrogen, oxygen, halogens, sulphur, and nitrogen, but the nitrogen must not be present as amide. The oxygen may be calculated from the following formula:

$$O\% = 2\cdot6666 \times C\% + (1 - 0\cdot21568 \times N\%/H\%) \times$$
$$7\cdot9369 \times H\% + 1\cdot497 \times S\% - 100 \times O'/E,$$

where E is the weight of substance and O' the quantity of oxygen yielded by the iodate; 6 molecules of iodate give 15 atoms of oxygen.   W. P. S.

Estimation of Nitrogen and Ammonia as Ammonium Chloride.

A. VILLIERS (*Bull. Soc. chim.*, 1919, [iv], **25**, 335—337. Compare A., 1918, ii, 332).—Further evidence is given showing that the loss in weight of ammonium chloride when heated in a narrow-necked, conical flask for four days at 105° is practically negligible (compare Auger, this vol., ii, 117).   W. G.

Volumetric Estimation of Phosphoric Acid by the Pincus Method, as applied to the Estimation of Magnesium.

J. W. SPRINGER (*Zeitsch. angew. Chem.*, 1919, **32**, 192).—The magnesium salt is precipitated as ammonium magnesium phosphate, the precipitate heated to boiling with ammonium acetate solution and water, and titrated with standardised uranyl acetate solution, using potassium ferrocyanide as an external indicator. [See, further, *J. Soc. Chem. Ind.*, 1919, August.]   W. P. S.

Microelementary Analysis.

E. DIEPOLDER (*Chem. Zeit.*, 1919, **43**, 353—354).—Methods are described for the estimation of nitrogen, carbon, hydrogen, and halogens in very small quantities (a few mg.) of substance; the first three elements mentioned are estimated by combustion, whilst halogens are estimated by the Carius method. [See, further, *J. Soc. Chem. Ind.*, 1919, August.]   W. P. S.

Micro-methods for the Determination of Carbon and Moisture in Minerals.

G. KARL ALMSTRÖM (*Svensk. Kem. Tidskrift*, 1919, **31**, 71—74).—Pregl's apparatus for combustion

and his potassium dichromate were applied to the estimation of carbon dioxide and moisture in minerals. The moisture values obtained in this way were too high. Vanadium pentoxide, having a low m. p. (660°), being strongly acid at high temperatures and combining with most substances to give readily fusible products, was thought to be a likely substitute that might give better results. The results for carbon dioxide were accurate, but the moisture values were still too high. Twenty to thirty mg. of the sample were used, and to this was added 0·2 to 0·3 gram of the oxidising agent. Neither can be rendered sufficiently free from moisture to yield trustworthy results. A Penfield apparatus made on a "micro" scale gives trustworthy figures when employed in the estimation of moisture in minute amounts of mineral sample.

CHEMICAL ABSTRACTS.

Cyanometric Method of Estimating Silver and Halogens in Ammoniacal Solution. J. EGGERT and LOTTE ZEPFEL (*Ber.*, 1919, **52**, [*B*], 1177—1185).—The procedure depends on the fact that silver iodide is only precipitated from very dilute ammoniacal solutions of silver salts by addition of potassium iodide when large amounts of electrolytes are present or when the solution is warmed, continuously shaken, or preserved for a long time; otherwise, an opalescence of colloidal silver iodide is formed. If potassium cyanide solution is added, the turbidity increases at first and suddenly disappears when the amount of CN′ necessary for the formation of Ag(CN)′$_2$ has been added. Silver is estimated in ammoniacal solution in the following manner. A known volume of approximately 0·1N-potassium cyanide solution is diluted with about four times its volume of water, and sufficient ammonia is added to make the solution at least 0·25N; after introduction of a quantity of potassium iodide approximately equivalent to that of the cyanide taken, the silver solution is added to incipient turbidity. Halogens are estimated indirectly by using an excess of silver nitrate solution and titration of the residual silver after filtration of the silver haloid. The method can also be applied for estimation of acids, the silver salts of which are distinguished by sufficient difference in their solubility in ammonia; thus, chloride and iodide may be simultaneously estimated in that their sum is determined by the indirect process and the iodide alone estimated in a solution which is sufficiently ammoniacal to retain the silver chloride in the dissolved state. To obtain accurate results, it is necessary that the amount of potassium iodide used as indicator should be approximately equivalent to the amounts of substance taken for titration.

The use of potassium iodide in Liebig's method of titration is shown to bring no advantage, and in certain cases even to lead to false results.   H. W.

Sensitive Reaction of Manganese Salts. H. CARON and D. RAQUET (*Ann. Chim. anal.*, 1919, [ii], **1**, 174).—A red

coloration is obtained when 10 c.c. of a manganese salt solution is treated with 2 c.c. of saturated potassium oxalate solution, 1 c.c. of acetic acid, and a few drops of potassium hypochlorite solution. The test will detect the presence of as little as 0·05 mg. of manganese in 10 c.c. of solution. Zinc salts do not interfere with the reaction, but iron salts must not be present.   W. P. S.

Estimation of Ferrous Iron by means of the Oxidation Potential.

I. M. KOLTHOFF (*Chem. Weekblad*, 1919, **16**, 450—461).—The ferrous solution, acidified with sulphuric or hydrochloric acid, is titrated with a standardised potassium dichromate solution. The *E.M.F.* between a platinised platinum electrode immersed in the solution and a normal calomel electrode is determined after successive additions of the dichromate solution, and the values obtained are plotted in a curve against the volume of the solution added. In the neighbourhood of the end-point, the *E.M.F.* increases rapidly, the exact end-point being given by the middle point of the nearly vertical curve section. Titration with potassium bromate gives satisfactory results, the end-point being sharper in hydrochloric than in sulphuric acid solution. With potassium permanganate solution, the value of the *E.M.F.* obtained is variable, increasing when the liquid is stirred.

W. S. M.

Estimation of Nickel in Ferro-nickels and Steels.

PAUL NICOLARDOT and GEORGES GOURMAIN (*Bull. Soc. chim.*, 1919, [iv], **25**, 338—344).—A comparison of the three methods of estimating nickel in nickel steels, namely: (1) electrolytic method; (2) precipitation with dicyanodiamidine; (3) precipitation with dimethylglyoxime. Method (2) gives results comparable with those of method (3), but needs much more care in its conduct. The results obtained by the use of dimethylglyoxime are invariably lower than by the electrolytic method, since in the latter method any cobalt present, and generally a little iron and manganese, are weighed in with the nickel. For rapid work, too, the dimethylglyoxime method is preferable, the precipitate being weighed on a tared filter paper.   W. G.

Estimation of Small Quantities of Antimony.

W. BEAM and G. A. FREAK (*Analyst*, 1919, **44**, 196—199).—When modified slightly, a method described by Schidrowitz and Goldsbrough (A., 1911, ii, 338) was found to be trustworthy. In this method, the antimony is deposited on a strip of copper, then dissolved in alkaline permanganate solution, and estimated colorimetrically as sulphide. The chief modifications introduced are the reduction of antimony solution with sulphur dioxide before the precipitation with hydrogen sulphide (this ensures the precipitation of the metal as its trisulphide, which is always the case in the comparison solution), and the use of 1% potassium hydroxide solution and a limited amount of potassium permanganate solution for the solution of the

deposited antimony.   [See, further, *J. Soc. Chem. Ind.*, 1919, 515A.]

W. P. S.

Estimation of Small Amounts of Benzene in Ethyl Alcohol.

F. W. BABINGTON and ALFRED TINGLE (*J. Ind. Eng. Chem.*, 1919, 11, 555—556).—One hundred c.c. of the alcohol are mixed with 200 c.c. of water and distilled, 20 c.c. of distillate being collected in a narrow, graduated tube having a capacity of 50 c.c. This distillate is treated with 15 c.c. of potassium dichromate solution (one-sixth saturated) and 2 c.c. of hydrochloric acid (D 1·12), the tube closed with a rubber stopper, and its contents mixed. After about fifteen minutes, the mixture is shaken with exactly 10 c.c. of light petroleum and the latter allowed to separate; the increase in volume of the petroleum gives the amount of benzene present. The method is trustworthy for quantities of benzene up to 0·75%.

W. P. S.

Chlorination of Benzene.   Analysis of Mixtures of Benzene, Chlorobenzene, and Dichlorobenzene, etc.   PERCY

F. FRANKLAND, S. RAYMOND CARTER, and DOROTHY WEBSTER (*J. Soc. Chem. Ind.*, 1919, **38**, 153—155).—The method described is similar in principle to that employed by Colman (A., 1915, ii, 184; *J. Soc. Chem. Ind.*, 1919, **38**, 57) for the estimation of the percentages of benzene, toluene, and xylene in commercial toluene. The sample (100 c.c.) is distilled from an Engler flask under uniform conditions, and the distillates are collected in measuring cylinders. Three fractions are obtained by interrupting the distillation at 122° (corr.) and again at 142° (corr.). The volumes of liquid which distil below 122° and above 142° are noted, and the percentages of benzene and chlorobenzene present in the original mixture are obtained from a graph which has been constructed from experiments with mixtures of known composition. The dichlorobenzene may be found by difference. The graph is only applicable to samples containing 50—80% of chlorobenzene and for those which contain such amounts of benzene and dichlorobenzene as yield not less than 5% or more than 50% either below 122° or above 142°; in cases where the sample does not fall within these limits, such measured volume of benzene, chlorobenzene, or dichlorobenzene is added that the resulting mixture comes within the specified limits. The graph was constructed by the use of pure *p*-dichlorobenzene, but it is found that the presence of *o*-dichlorobenzene does not materially affect the accuracy of the process even if it forms about 40% of the total dichlorobenzene present in the mixture. Benzene hexachloride, if present, should be filtered before distillation, and the quantity then remaining in solution is too small to influence the analysis; if its percentage is required, it is allowed to separate at the ordinary temperature from the fraction, b. p. above 140°, collected, washed with light petroleum (b. p. 65°), and dried. The mother liquor is concentrated, and the second crop similarly treated and weighed with the first lot of benzene hexachloride.   H. W.

Estimation of Monochlorobenzene in Mixtures containing Benzene, Monochlorobenzene, and Dichlorobenzene. N. G. S. COPPIN and F. HOLT (*Analyst*, 1919, **44**, 226—229).—A method of estimating monochlorobenzene in crude chlorinated benzene has been based on Northall-Laurie's method of estimating toluene in commercial toluene (A., 1915, ii, 703). A known volume of the sample is distilled, the first quarter of the distillate collected, a further half then distilled, and the residual quarter left in the flask. The boiling points of the first fraction and of the residue are determined in the special apparatus devised by Northall-Laurie, and from these results, by reference to a graph constructed from the results obtained with mixtures of known composition, the amount of monochlorobenzene in the sample is found. The graph is made by plotting the results obtained with weighed quantities of benzene, monochlorobenzene, and *p*-dichlorobenzene, the boiling points of the first fractions forming the ordinates and those of the residues the abscissæ. Small amounts of *o*-dichlorobenzene and trichlorobenzene are also formed when benzene is chlorinated, but not in sufficient quantity to have a material influence on the results. [See, further, *J. Soc. Chem. Ind.*, 1919, August.]

C. A. M.

A Revision of the Copper Phosphate Method for the Titration of Sugar. OTTO FOLIN and EUGENE C. PECK (*J. Biol. Chem.*, 1919, **38**, 287—291).—Variable results were encountered with this method when salt mixtures prepared from the same lot of chemicals by different individuals were employed. It was ascertained that, in order to obtain concordant results, great care must be taken to prepare the salt mixture correctly. The preparation of this mixture is described in detail. The method of Folin and McEllroy (A., 1918, ii, 207) could, however, be justly criticised on the ground that reduction of the copper sulphate by the thiocyanate may occur. By rendering the copper sulphate solution alkaline before adding the thiocyanate, this reduction is prevented. The modified process is as follows: 5 c.c. of the 5·9%·copper sulphate solution are placed in a test-tube and rendered alkaline by the addition of 1 c.c. of saturated sodium carbonate. Four to five grams of the phosphate–carbonate–thiocyanate mixture are now added, and the whole is heated until the salts have dissolved. The titration is then carried out as described in the original method.

J. C. D.

Micro-estimation of Sugar in Blood. A. KOWARSKY (*Deut. med. Woch.*, 1919, **45**, 188—190; from *Chem. Zentr.*, 1919, ii, 475).—The method depends on Bertrand's process, which consists in boiling the sugar solution with alkaline cuprous oxide solution, separating the precipitated copper oxide from the solution, and dissolving it in acidified iron sulphate solution; the ferrous oxide formed (equivalent to the cuprous oxide) is titrated with permanganate. To avoid loss when working with small quantities of

sugar, a known weight of the latter is added to the cuprous solution, which is subsequently deducted from that found experimentally. The method permits an exact estimation of sugar (to 0·01%) in 0·35 c.c. of blood, and can also be used for determining sugar in urine. It is particularly useful in diagnosis of disease of the kidneys, in which only small quantities of urine are frequently available; an exact estimation can be made with 0·1 c.c. of urine.

H. W.

New Method for the Estimation of Oxalic Acid. Hugo Krause (Ber., 1919, **52**, [B], 1222—1223. Compare this vol., ii, 203).—A reply to Ott (this vol., ii, 303).   H. W.

Methods for the Quantitative Estimation of Hippuric Acid. New, Simple, and Accurate Method. Eduardo Filippi (Arch. Farm. Sperim. sci. aff., 1918, **26**, 243—256; from Chem. Zentr., 1919, ii, 472).—A review of the previous methods is given, but the results obtained by them are not satisfactory. A simple method has therefore been elaborated based on the observation of Pelouze, that hippuric acid is converted into benzoic acid when boiled with sulphuric acid and manganese dioxide. Urine (300—500 c.c.) is concentrated to 100 c.c. and extracted during two hours at 60—65° with a mixture of benzene (2 volumes) and alcohol-free ether (1 volume); after removal of the solvent, the residue is heated under a reflux condenser, gently at first, but finally more strongly, with sulphuric acid (20 c.c.) and manganese dioxide (3–4 grams) during one and a-half hours. The product is distilled with steam, and the distillate is thoroughly extracted with ether. The benzoic acid left after removal of the ether is weighed.   H. W.

Micro-estimation of Fat. E. and (Mrs.) F. Weehuizen (Pharm. Weekblad, 1919, **56**, 810—822).—A criticism of the method of Ivar Bang for the estimation of fat in small quantities of blood (Methoden zur Mikrobestimmung einiger Blutbestandteile). The following improvement of the method is proposed: About 0·3 gram of blood is absorbed in two or three pieces of filter paper (16 mm. × 26 mm.), and the weight determined in a torsion balance. The papers are dried in a vacuum and then placed in a test-tube (2·5 cm. × 16 cm.) with about 7 c.c. of alcohol. The tube is suspended in a water-bath at 90°, and the alcohol boiled for five minutes. The solution is transferred to a pointed centrifuge tube (1·5 × 10 cm.) and evaporated to 2·5 c.c. in a water-bath. The papers are extracted again with 8 c.c. of alcohol, and the solution is added to the centrifuge tube, in which the volume is again reduced to 2·5 c.c. In both cases, evaporation is expedited by passing hydrogen through a capillary tube into the liquid. Five drops of $N/2$-sodium hydroxide solution are now added, and the evaporation is continued until the volume is reduced to 0·3 c.c. As the duration of the saponification must be at least twenty

minutes, it may be necessary to add ten drops of alcohol and a drop of water when a volume of $\frac{1}{4}$ c.c. is reached. The residue, which must be free from alcohol, is made up to 5 c.c. and is transferred to a micro-burette. The solution is used to titrate 1 c.c. of the standard calcium chloride solution until a permanent froth is obtained. The standard solution is prepared by adding 5·9 c.c. of N/10-calcium chloride solution to 13 grams of sodium chloride and making up to 1 litre. One c.c. of this solution is equivalent to 0·312 mg. of triolein.   W. S. M.

Schiff's Reaction for the Detection of Carbamide.

DOMENICO GANASSINI (*Arch. Farm. sperim. sci. aff.*, 1918, **26**, 238—242; from *Chem. Zentr.*, 1919, ii, 473).—Schiff's reaction does not occur with pure furfuraldehyde. Acetone was found to be the active constituent of an efficient sample of furfuraldehyde. The reaction is obtained with certainty with a reagent of the following composition: furfuraldehyde (5 drops), acetone (2 c.c.), water (2 c.c.), and concentrated hydrochloric acid (1 c.c.). When a small quantity of this reagent is added to a minimal amount of carbamide, a pink coloration is gradually developed which becomes red and then intensely purple, and later brown. If acetone is replaced by other substances containing the COMe-group, such as ethyl acetate, acetaldehyde, acetylacetone, or pyruvic acid, red to violet colorations are more or less slowly developed, which, however, are indefinite and not to be compared with the beautiful coloration in the presence of acetone.   H. W.

Estimation of the Amylolytic Power of Saliva.

L. GRIMBERT (*J. Pharm. Chim.*, 1919, [vii], **19**, 244—250).—A quantity of air-dried potato starch equivalent to 5 grams of dry starch is boiled for two minutes with 100 c.c. of water, then cooled, 4 c.c. of filtered saliva are added, and the mixture is kept at 37° for one hour; it is then heated at 100° for ten minutes, cooled, diluted to 200 c.c., filtered, and the maltose is estimated in the filtrate. The amount of maltose is multiplied by 0·9473 to give the quantity of starch saccharified, and this, expressed as a percentage of the total starch, gives the amylolytic power of the saliva; for normal saliva, it lies between 73 and 74.   W. P. S.

Value of Some New Colour Reactions of Urine.

ALEX. SKUTETZKY and M. KLAFTEN (*Wien. klin. Woch.*, 1918, **31**, 1016—1018; from *Chem. Zentr.*, 1919, ii, 8).—The reactions proposed by Russo (methylene-green reaction), Wiener, and Kronberger have been critically examined; in each case, the coloration observed is due to simple physico-chemical causes, and does not depend on chemical processes. The reactions are consequently without diagnostic value.   H. W.

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LXXXI.—*A New Photographic Phenomenon.*

By DONALD NEIL MCARTHUR and ALFRED WALTER STEWART.

ALTHOUGH the phenomenon here described has not yet been entirely elucidated, the present preliminary note appears to be justified by the results which have already been obtained. A sensitive photographic plate is placed, film upward, at the bottom of a light-tight box; on the film are placed two or more glass microscope slides, and resting on these supports is laid a negative, also film side upward. The box is then closed and is placed in the neighbourhood of a Bunsen burner, a bat's-wing flame, or an electrical kettle-heater. After an exposure of some hours, the plate after development shows an image of the negative. The resulting photograph is the reverse of the original negative, that is, it is a positive such as would be obtained by simple printing with sensitised paper in the usual way.

In the experiments made, the plates used have been Wellington Anti-screen, Imperial Extra Rapid and Imperial Sovereign makes, different batches of each kind having been employed.

The material of the box may be either wood or cardboard. Care has been taken that no light enters the box; certain of the experiments having been conducted in total darkness, whilst in other cases the openings between the two halves of the boxes have been carefully sealed. The results are obtained whether the box is left in the open air or is enclosed in an air-tight desiccator.

The nature of the source of heat appears to exercise some influence on the rapidity with which the effects are produced. Very poor results are yielded by a Meker burner; poor results are given by a Bunsen flame impregnated with calcium salts; with lithium or sodium salts, the effects are more strongly marked. The electric heater gives very good results when worked on its lower resistance.

The distance between the box and the source of heat has usually been about 30—45 cm., but on one occasion results were obtained with a box placed in a cupboard 180 cm. away from a sodium burner, although in this case the exposure was an extremely prolonged one.

The most striking peculiarity of these experiments is the fact that when the box is arranged so that the sensitive plate lies between the source of heat and the negative, the results are obtained just as sharply as if the negative had been interposed between the heater and the sensitive plate. Were direct-acting rays concerned in the matter, it seems clear that in these circum-

stances the plate would be fogged by their passage through it before they reached the negative at all.

The results are not due to any radioactive material in the neighbourhood, for one of us carried out test experiments in the laboratory of the Queen's University of Belfast, where no radioactive contamination exists, and the effects were obtained there also.

The effects cannot be ascribed to the negative having stored up light which it liberates again in the dark, for a parallel experiment made with a negative which had been specially illuminated for ten minutes within 15 cm. of a spectroscopic spark apparatus gave no results when no source of heat was present.

The rays which produce the effects on the sensitive plate appear to be similar in properties to light rays. Glass is practically transparent to them; inkstains, seccotine, and metal show different degrees of opacity. It has been found that the rays can be diffracted and refracted just like ordinary light.

The matter is being further investigated, but the foregoing is sufficient to show that an interesting field has been opened up.

THE PHYSICAL CHEMISTRY LABORATORY,
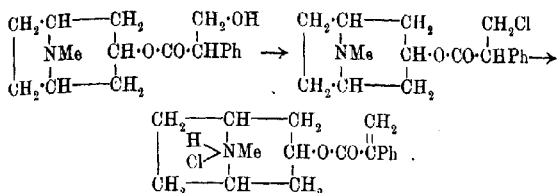GLASGOW UNIVERSITY.   [Received, June 2nd, 1919.]

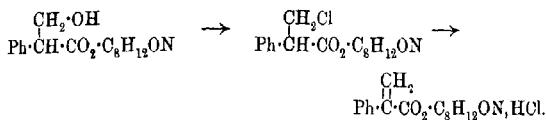# LXXXII.—*The Stereochemistry of Hyoscine.*

By HAROLD KING.

IN a former communication (this vol., p. 476), it was shown that by resolution of a weakly active hyoscine by means of d-a-bromo-π-camphorsulphonic acid, d-hyoscine bromocamphorsulphonate was obtained as the more sparingly soluble salt. The base proved to be the enantiomorph of the therapeutically valuable l-hyoscine of commerce. The unexpected discovery was made, however, that d- and l-hyoscines gave dl-oscine on hydrolysis with acid or alkali, whereas benzoyl-d-oscine under similar conditions gave optically pure d-oscine. Furthermore, the d- and l-oscine bases prepared by resolution of dl-oscine were not racemised by acid or alkali. On these grounds, d- and l-hyoscines were regarded as partially racemic esters, the optical activity being solely conditioned by the activity of the tropyl radicle.

In the present communication, further confirmatory evidence is adduced. In 1908, Wolffenstein and Mamlock (*Ber.*, **41**, 730) showed that atropine (tropyltropine) can be converted into

β-chlorohydratropyltropine, and that, on evaporation of the ethereal solution of this base, an intramolecular change takes place, hydrogen chloride being transferred from carbon to nitrogen, with the formation of *apo*atropine hydrochloride.

$$
\begin{array}{ccc}
CH_2\cdot CH\!\!-\!\!-\!\!CH_2 & CH_2\cdot OH & CH_2\cdot CH\!\!-\!\!-\!\!CH_2 \quad CH_2Cl \\
|\quad NMe\quad CH\cdot O\cdot CO\cdot CHPh & \rightarrow & |\quad NMe\quad CH\cdot O\cdot CO\cdot CHPh\!\!\rightarrow \\
CH_2\cdot CH\!\!-\!\!-\!\!CH_2 & & CH_2\cdot CH\!\!-\!\!-\!\!CH_2
\end{array}
$$

$$
\begin{array}{c}
CH_2\!\!-\!\!-\!\!CH\!\!-\!\!-\!\!CH_2 \quad CH_2 \\
\underset{Cl}{\overset{H}{>}}NMe \quad CH\cdot O\cdot CO\cdot CPh \; . \\
CH_2\!\!-\!\!-\!\!CH\!\!-\!\!-\!\!CH_2
\end{array}
$$

Willstätter and Hug (*Zeitsch. physiol. Chem.*, 1912, **79**, 146) showed that, in a precisely similar manner, *l*-hyoscine on treatment with thionyl chloride gave β-chlorohydratropyloscine hydrochloride, and the ethereal solution of the base, on evaporation, gave *apo*hyoscine (*apo*scopolamine) hydrochloride.

$$
\begin{array}{ccc}
CH_2\cdot OH & & CH_2Cl \\
Ph\cdot CH\cdot CO_2\cdot C_8H_{12}ON & \rightarrow & Ph\cdot CH\cdot CO_2\cdot C_8H_{12}ON \quad \rightarrow
\end{array}
$$

$$
\begin{array}{c}
CH_2 \\
Ph\cdot C\cdot CO_2\cdot C_8H_{12}ON,HCl.
\end{array}
$$

This reaction destroys the asymmetry of the tropyl group, and could it be carried out under mild conditions, so as to preclude hydrolysis and racemisation, it should indicate whether the oscine portion of the molecule is active or inactive in *l*-hyoscine. Willstätter and Hug, apparently unaware of the significance of this reaction, did not record the polarimetric examination of *apo*hyoscine. Moreover, they used potassium carbonate for liberating the bases from their salts, this alkali being known to racemise *l*-hyoscine partly if contact is at all prolonged (Schmidt, *Arch. Pharm.*, 1898, **47**, 236), and their yield of *apo*hyoscine was only 50 per cent., the loss being attributed to hydrolysis. It has now been found that, on replacing potassium carbonate by the much weaker alkali sodium hydrogen carbonate, the reaction proceeds quantitatively throughout, and the resulting *apo*hyoscine is optically inactive.

To complete the proof of the partial racemic ester nature of *l*-hyoscine, the resolution of *apo*hyoscine has been attempted.

apo*Hyoscine camphorsulphonate* (m. p. 157—158°) is a very readily soluble salt which can be recrystallised from a mixture of alcohol and ether, but shows no signs of resolution. The bromocamphorsulphonate was not obtained crystalline, but the

d-hydrogen tartrate crystallises well from water. It contains two molecules of water of crystallisation, melts at 95—97°, and has $[a]_D + 8.6°$ in water. Repeated crystallisation failed to change its melting point or its specific rotation.

The results so far obtained are best explained on the assumption already made that *d-* and *l*-hyoscines are partially racemic esters, *d*-hyoscine being composed of *d*-tropyl-*d*-oscine and *d*-tropyl-*l*-oscine, whilst *l*-hyoscine contains the enantiomorphs. Although *d*-hyoscine is not further resolved by *d-a*-bromo-π-camphorsulphonic acid, it does not follow that *l*-hyoscine is not resolvable by the same acid, or that either base is not resolvable by other optically active acids. The behaviour of pure *d-* and *l*-hyoscines towards the optically active acids, *d*-camphor-β-sulphonic, *d-a*-bromo-π-camphorsulphonic, and *d*-tartaric has now been investigated, but in no case was there any indication of resolution. The *d*-hydrogen tartrate of *d*-hyoscine could only be obtained as an uncrystallisable syrup.

The properties of the various crystalline camphorsulphonates are shown in the following table:

	d-Camphor-β-sulphonate.			d-a-Bromo-π-camphorsul-phonate.		
	M. p.	[M]$_D$ salt.	[M]$_D$ basic ion (calc.).	M. p.	[M]$_D$ salt.	[M]$_D$ basic ion (calc.).
d-Hyoscine	175—177°	+156.7°	+106.3°	158—160°	+370.5°	+91.8°
l-Hyoscine	186—187°	−40.8°	−91.2°	169—170°	+172.4°	−106.3°

The value obtained by direct observation on *d-* or *l*-hyoscine hydrobromides was $[a]_D \pm 33°$ or $[M]_D \pm 100°$ (this vol., pp. 503, 504).

A peculiar numerical relationship is observable in the calculated molecular rotatory powers of the basic ions, the significance of which is not clear. It suggests a further resolution of *d-* and *l*-hyoscines, but, apart from these values, there is no evidence to support it, the picrate, for instance, prepared from *d*-hyoscine camphorsulphonate, being identical with that prepared from *d*-hyoscine bromocamphorsulphonate.

In addition to the above salts, *l*-hyoscine was found on one occasion to form a labile salt with *d-a*-bromo-π-camphorsulphonic acid. This salt melted at about 150° and had $[a]_D + 25.5°$, $[M]_D + 157°$, but it was not obtained quite pure, as after two crystallisations it became transformed into the ordinary form of higher melting point (169—170°), and subsequent attempts to reproduce it were unsuccessful. Whether the tautomerism is centred in the bromocamphorsulphonic acid portion of the molecule, as has only rarely been observed (Kipping and Tattersall, T., 1903, **83**, 918), or in the hyoscine portion of the molecule, must

for the present remain undecided. In this connexion, however, it is possibly significant that Wentzel (*Dissertation*, cited by Hesse, *J. pr. Chem.*, 1901, [ii], **64**, 274), by crystallising *l*-hyoscine hydrobromide from alcohol, obtained a lævo-hyoscine hydrobromide of much higher rotatory power, namely, $[\alpha]_D - 32\cdot9°$, which fell, on keeping, to $- 25\cdot8°$, the usually observed value. Hesse (*ibid.*, 353) claims to have partly substantiated this observation. This enhanced value for the anhydrous *l*-hyoscine hydrobromide gives a calculated value $[\alpha]_D + 24\cdot8°$ for the *d*-*a*-bromo-π-camphorsulphonate, a value of the same order as that observed, $[\alpha]_D + 25\cdot5°$, for the labile bromocamphorsulphonate described above.

The present author has obtained another *l*-hyoscine bromocamphorsulphonate, $[\alpha]_D + 17\cdot9°$, m. p. 200°, during the resolution of a weakly active hyoscine by means of α-bromo-π-camphorsulphonic acid. The amount of material was, however, only sufficient to prove the identity of the *l*-hyoscine. It is not improbable that the acid contained in this salt is an isomeric acid which was present as an impurity in the original ammonium α-bromo-π-camphorsulphonate used.

EXPERIMENTAL.

Preparation of dl-apo*Hyoscine from* l-*Hyoscine.*

The method employed for preparing this base is a modification of that given by Willstätter and Hug (*loc. cit.*).

l-Hyoscine hydrobromide (3·87 grams) was converted into the base by the use of sodium hydrogen carbonate and chloroform. The chloroform-free base was warmed gently with 10 c.c. of thionyl chloride. The reaction proceeded smoothly, and, after keeping the product overnight, the thionyl chloride was distilled off under diminished pressure, and the last traces were removed by repeated extraction and evaporation with ether. The β-chlorohydratropylscine hydrochloride was dissolved in a little water, the solution rendered alkaline with sodium hydrogen carbonate, and the base thoroughly extracted with ether. Unlike *l*-hyoscine, this chlorosubstituted base could be readily extracted. The ethereal solution was evaporated to dryness, leaving a pale yellow oil, which immediately became opalescent, and, on digesting on the water-bath with fresh ether, no longer dissolved, but commenced to crystallise at the edges. On keeping for two days, it had crystallised completely in rosettes of stout needles consisting of *apo*hyoscine hydrochloride.

A 2·5 per cent. aqueous solution was neutral to litmus, and when examined in a 2-dcm. tube proved to have no action on the plane of polarised light.

The salt (2·7 grams) was dissolved in water (15 c.c.), the solution rendered alkaline with sodium hydrogen carbonate, and the base completely extracted with ether. On removal of the solvent, the base crystallised readily in rhomboidal plates. It melted at 75—78°, and amounted to 2·4 grams. Theory requires 2·5 grams. It was recrystallised from light petroleum (b. p. 40—60°), and separated in magnificent rhomboidal plates. The yield was 2·2 grams, and the base now melted at 79—80° (79—80° corr.).

The base was examined in 2·5 per cent. solution in absolute alcohol in a 2-dcm. tube, but was quite inactive.

Willstätter and Hug record the melting point 97° for *apo*hyoscine base, but this appears to be a misprint for 79°, as the nitrate, picrate, and aurichloride were found to melt at 157° (decomp.), 217—218°, and 188° respectively, in substantial agreement with Willstätter and Hug's recorded values, 157°, 217°, and 183—184° respectively. The appearance and solubilities of the base and these salts were also in agreement. (Aurichloride.— Found: $Au = 31·5$. $C_{17}H_{19}O_3N,AuCl_3,HCl$ requires $Au = 31·5$ per cent.).

dl-apo*Hyoscine Camphor-β-sulphonate.*

*apo*Hyoscine base was converted into its salt with camphor-β-sulphonic acid. It crystallised from a mixture of absolute alcohol and ether in irregular-shaped leaflets. It was recrystallised twice, yielding, finally, 0·65 gram melting at 157—158° (160·5—161·5° corr.).

The specific rotation was determined in water.

$c = 2·069$; $l = 2$-dcm.; $\alpha + 0·404°$; $[\alpha]_D + 9·76°$; $[M]_D + 50·5°$.

The value of $[M]_D$ is in excellent agreement with that recorded by Graham (T., 1912, **101**, 747), namely, $[M]_D + 50·4°$ for the camphorsulphonic acid ion. That there was no resolution was confirmed by extracting the base from the solution, which had been used for determining the rotatory power, after rendering alkaline with sodium hydrogen carbonate and examining the solution of the base in absolute alcohol. It had no effect on the plane of polarised light.

The salt with d-α-bromo-π-camphorsulphonic acid was not obtained crystalline.

dl-apo*Hyoscine d-Hydrogen Tartrate.*

One gram of *apo*hyoscine nitrate was regenerated to base, using sodium hydrogen carbonate and ether. The d-hydrogen tartrate

of the base was prepared in aqueous solution by combination with one equivalent proportion (0·45 gram) of d-tartaric acid. On concentrating the solution to about 10 c.c., apohyoscine d-hydrogen tartrate crystallised in clusters of radiating, white needles. The product was collected and washed with water. When dried in the air, it amounted to 1·15 grams. It was recrystallised four times from water, the properties of the successive fractions being as follows:

I.	1·15 grams,	m. p.	97°,	$[a]_D + 8·74°.$
II.	1·0 gram,	,,	95—97°,	$[a]_D + 8·35°.$
III.	0·75 ,,	,,	95—97°,	$[a]_D + 7·78°.$
IV.	0·45 ,,	,,	95—97°,	$[a]_D + 8·59°.$

Employing Landolt's value, $[M]_D + 42·84°$, for ammonium hydrogen tartrate, the calculated value for dl-apohyoscine d-hydrogen tartrate is $[a]_D + 9·1°$, in approximate agreement with the values recorded above. The base when recovered from the fourth fraction was examined in absolute alcohol, but the solution was devoid of optical activity.

dl-apo$Hyoscine$ d-$hydrogen tartrate$ is sparingly soluble in cold, but dissolves freely in hot water. It crystallises with two molecular proportions of water in clusters of long needles. In a capillary tube it melts at 95—97° (95—97° corr.), and effervesces at 115°, but it melts below 90° when exposed on a watch-glass to a temperature of 90—95°. The water of crystallisation is not lost when the salt is dried in a vacuum over sulphuric acid:

0·1037, air-dried, gave 0·2031 CO_2 and 0·0579 H_2O. C = 53·4; H = 6·2.

$C_{17}H_{19}O_3N,C_4H_6O_6,2H_2O$ requires C = 53·5; H = 6·2 per cent.

The specific rotation was determined in dilute aqueous solution, using the air-dried salt.

$c = 2·008$; $l = 2$-dcm.; $a + 0·345°$; $[a]_D + 8·6°$; $[M]_D + 40·5°.$

d-$Hyoscine$ $Camphor$-β-$sulphonate$.

Almost pure d-hyoscine base (1·5 grams) was neutralised with camphor-β-sulphonic acid (1·15 grams). The syrupy salt was obtained crystalline by boiling with anhydrous ethyl acetate. It amounted to 2·3 grams and had $[a]_D + 27·6°$. It was recrystallised thrice more from anhydrous ethyl acetate, the specific rotation of the three fractions being successively $[a]_D + 29·5°$, $+ 29·4°$, $+ 29·3°$. The final fraction amounted to 1·5 grams.

d-$Hyoscine$ $camphor$-β-$sulphonate$ crystallises well from anhydrous

ethyl acetate, in which it is sparingly soluble, in elongated, hexagonal-shaped leaflets or in acicular needles. Each fraction examined appeared to contain one molecule of water, which was lost at 95°. The anhydrous salt melted at 175—177° (179—181° corr.).

For the first crops of successive crystallisations, the percentage losses at 95° were 2·95, 3·33, 1·9, 2·95.

$C_{17}H_{21}O_4N,C_{10}H_{16}O_4S,H_2O$ requires $H_2O = 3·25$ per cent.

0·1055, dried at 95°, gave 0·2339 CO_2 and 0·0663 H_2O. C = 60·5; H = 7·0.

$C_{17}H_{21}O_4N,C_{10}H_{16}O_4S$ requires C = 60·5 ; H = 7·0 per cent.

The specific rotatory power of the anhydrous salt was determined in water.

$c = 1·994$; $l = 2$-dcm. ; $a + 1°10'$; $[a]_D + 29·25°$; $[M]_D + 156·7°$.

Employing the value $[M]_D + 50·4°$ for the camphor-β-sulphonic acid ion, the calculated molecular rotation of the d-hyoscinium ion is $[M]_D + 106·3°$, whence $[a]_D + 34·9°$. The value found by direct observation of d-hyoscine hydrobromide was $[a]_D + 33·2°$ (this vol., p. 503).

The picrate prepared from the four times recrystallised camphor-β-sulphonate by double decomposition was identical with d-hyoscine picrate obtained from d-hyoscine a-bromo-π-camphorsulphonate.

d-Hyoscine d-hydrogen tartrate was prepared, but all attempts to crystallise it failed.

l-*Hyoscine Camphor-β-sulphonate.*

Pure l-hyoscine base (1·4 grams) was neutralised in aqueous solution with Reychler's camphorsulphonic acid (1·0 gram). The dehydrated, syrupy salt was dissolved in anhydrous ethyl acetate, and, on keeping, crystallised homogeneously in clusters of large plates. The salt, when collected, amounted to 1·7 grams, melted at 187—188°, and had $[a]_D - 7·2°$. It was recrystallised twice more, the melting point remaining the same and the rotation being virtually unaltered with $[a]_D - 8·1°$ and $[a]_D - 7·6°$ successively.

l-*Hyoscine camphor-β-sulphonate* crystallises from anhydrous ethyl acetate in transparent, rectangular plates. It melts at 186—187° (190—191° corr.):

0·2181, dried at 95°, lost nil.

0·0951 gave 0·2117 CO_2 and 0·0588 H_2O.   C = 60·7 ; H = 6·9.

$C_{17}H_{21}O_4N,C_{10}H_{16}O_4S$ requires C = 60·5 ; H = 7·0 per cent.

The specific rotation was determined in water.

$c = 2·006$; $l = 2$-dcm. ; $a - 18·33'$; $[a]_D - 7·6°$; $[M]_D - 40·8°$.

whence is calculated $[M]_D$ for l-hyoscinium ion $-91\cdot2°$ and $[a]_D -30\cdot0°$.

l-Hyoscine d-α-*Bromo-π-camphorsulphonate*.

This salt crystallises from anhydrous ethyl acetate in minute needles. The rotation is unchanged after repeated crystallisation, $5\cdot3$ grams having $[a]_D +28\cdot28°$ yielding, finally, $1\cdot8$ grams having $[a]_D +28\cdot05°$. It melts, when dried at 110°, at 169—170° (172·5—173·5° corr.). It is deliquescent in a damp atmosphere, and then crystallises in microscopic, rectangular leaflets, probably a hydrated form. The anhydrous salt was analysed, with the following result:

0·2168, dried at 95°, lost 0·0003. Loss = 0·1 per cent.

0·0997, „ 95°, gave 0·1934 CO_2 and 0·0538 H_2O. $C = 52·9$; $H = 6·0$.

$C_{17}H_{21}O_4N,C_{10}H_{15}O_4BrS$ requires $C = 52·7$; $H = 5·9$ per cent.

The specific rotation was determined in water.

$c = 2·026$; $l = 2$-dcm.; $a +1°8·2'$; $[a]_D +28·05°$; $[M]_D +172·4°$.

This gives a value $[M]_D -106·3°$ for the molecular rotation of the l-hyoscinium ion and $[a]_D -34·9°$.

Labile Salt.--On one occasion, a labile form of l-hyoscine bromocamphorsulphonate was isolated, the exact conditions being as follows. $7·5$ Grams of freshly prepared, syrupy l-hyoscine bromocamphorsulphonate were repeatedly evaporated to dryness under diminished pressure with absolute alcohol in order to remove all adhering water. The residue, freed as completely as possible from absolute alcohol, was then dissolved in anhydrous ethyl acetate, and, on keeping for two days, a mixture of two salts separated in what appeared to be approximately equal proportions. One salt had the characteristic crystalline appearance of l-hyoscine *d*-α-bromo-π-camphorsulphonate described above, but the other formed tufts of much larger needles with a more glistening appearance. A trace of each was removed, when the former melted at 169—170°, and was thus ordinary l-hyoscine bromocamphorsulphonate, whilst the second melted, either air-dried or dried at 100°, at 150°. The whole of the deposit was collected and recrystallised from ethyl acetate. It separated overnight in tufts of silky needles, which melted at 150°, but was contaminated by a much smaller proportion, this time, of ordinary l-hyoscine bromocamphorsulphonate, easily discernible as smaller, white tufts of needles. The product amounted to 3·6 grams.

$c = 2·068$; $l = 2$-dcm.; $a +1°3·4'$; $[a]_D +25·5°$.

o o*

This value is distinctly less than $[\alpha]_D + 28\cdot0°$ observed for ordinary l-hyoscine bromocamphorsulphonate. The product was again recrystallised, but gave the ordinary form of l-hyoscine bromocamphorsulphonate melting at 169—170°. All attempts again to isolate this labile salt from this particular batch of material were unsuccessful.

l-*Hyoscine Bromocamphorsulphonate*, m. p. 200°.

By resolution of a weakly active hyoscine by d-α-bromo-π-camphorsulphonic acid (this vol., p. 502), it was shown that the more sparingly soluble salt was d-hyoscine α-bromo-π-camphor-sulphonate, and that from the mother liquors a deliquescent salt having a specific rotation approximating to that of a l-hyoscine d-α-bromo-π-camphorsulphonate could be isolated.

The final mother liquor, on prolonged keeping at a low temperature, deposited 1·65 grams (1·6 per cent. yield) of a salt crystallising in rosettes of rectangular leaflets. It was not deliquescent and melted at 199—200° (203—204° corr.).

The specific rotation was determined on material dried at 95°.

$$c = 1\cdot943; \; l = 2\text{-dcm.}; \; \alpha + 41\cdot7'; \; [\alpha]_D + 17\cdot9°.$$

0·1028 gram, dried at 95°, gave 0·1994 CO_2 and 0·0553 H_2O.

$$C = 52\cdot9; \; H = 6\cdot0.$$

$C_{17}H_{21}O_4N, C_{10}H_{15}O_4BrS$ requires $C = 52\cdot7; \; H = 5\cdot9$ per cent.

0·1 Gram of this salt was converted into the picrate, which amounted to 0·09 gram and melted at 183—186°. On recrystallisation, it gave 0·08 gram melting at 185—186°, and when mixed with l-hyoscine picrate, no depression in the melting point was observed.
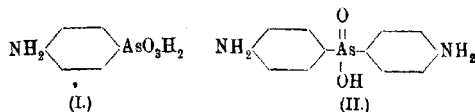
WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.   [*Received, June 27th*, 1919.]

LXXXIII.—*Substituted Phenylarsinic Acids and their Reduction Products, and the Estimation of Arsenic in such Compounds.*
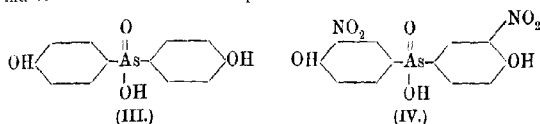
By ROBERT GEORGE FARGHER.

IN the preparation of p-aminophenylarsinic acid (I) by Béchamp's method (*Compt. rend.*, 1863, **56**, 1173), Pyman and Reynolds (T., 1908, **98**, 1180) isolated as a by-product a small proportion of
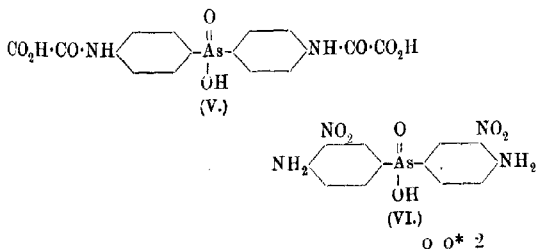
is-*p*-aminophenylarsinic acid (*pp'*-diaminodiphenylarsinic acid)
II).

$$NH_2\langle\quad\rangle AsO_3H_2 \qquad NH_2\langle\quad\rangle \overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{As}}\langle\quad\rangle NH_2$$

<div align="center">(I.)   (II.)</div>

In view of the close relation existing between the two acids and
he importance of the former as the starting point for the pre-
>aration of salvarsan, it seemed to be of interest to prepare the
corresponding 3 : 3'-*dinitro*-4 : 4'-*dihydroxydiphenylarsinic acid* (IV)
ind to examine its reduction products.

$$OH\langle\quad\rangle\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{As}}\langle\quad\rangle OH \qquad OH\langle\overset{NO_2}{\quad}\rangle\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{As}}\langle\overset{NO_2}{\quad}\rangle OH$$

<div align="center">(III.)   (IV.)</div>

For the preparation of this acid, the two methods described for
3-nitro-4-hydroxyphenylarsinic acid (Bertheim, *Ber.*, 1911, **44**,
3092; Benda and Bertheim, *loc. cit.*, 3445; Benda, *loc. cit.*, 3449)
can be used. In the first, the amino-acid (II) is converted into
the corresponding hydroxy-acid (III) (Benda, *Ber.*, 1908, **41**, 2371)
and subsequently nitrated under suitable conditions. This method
gives excellent results. In the second, the amino-acid is converted
into its *oxalyl* derivative (V), which is nitrated, the oxalyl group
removed by acid hydrolysis, and the amino-group in the resulting
3 : 3'-*dinitro*-4 : 4'-*diaminodiphenylarsinic acid* (VI) subsequently
replaced by hydroxyl by alkaline hydrolysis. The usefulness of
this method is marred, however, by the fact that at temperatures
approaching 140°, oxalic acid causes fission of the molecule of
pp'-diaminodiphenylarsinic acid to some extent, the product being
a mixture from which the *pp'*-dioxalylaminodiphenylarsinic acid
can be isolated by means of the sparing solubility of its barium
salt in cold dilute ammoniacal solution.

$$CO_2H\cdot CO\cdot NH\langle\quad\rangle\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{As}}\langle\quad\rangle NH\cdot CO\cdot CO_2H$$

<div align="center">(V.)</div>

$$NH_2\langle\overset{NO_2}{\quad}\rangle\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{As}}\langle\overset{NO_2}{\quad}\rangle NH_2$$

<div align="center">(VI.)</div>

<div align="right">0 0* 2</div>

Bertheim (*Ber.*, 1915, **48**, 352), who described the preparation and reduction of 3-nitro-4-hydroxyphenylmethylarsinic acid (VII), found that the direct reduction of the nitro-acid with sodium hyposulphite led to an impure product, whilst if the hyposulphite reduction were stopped at the amino-acid stage and the reduction continued with hypophosphorous acid, 3:3'-diamino-4:4'-dihydroxydiphenyldimethyldiarsine (VIII) was obtained.


(VII.)   (VIII.)
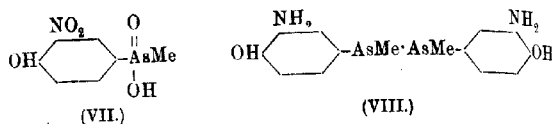
In the case of 3:3'-dinitro-4:4'-dihydroxydiphenylarsinic acid, complete reduction with sodium hyposulphite leads to 3:3'-diamino-4:4'-dihydroxydiphenylarsenious hydroxide (IX), for the crude, sparingly soluble reduction product, dissolved in methyl alcohol containing hydrochloric acid and precipitated with concentrated hydrochloric acid, gives rise to 3:3'-diamino-4:4'-dihydroxydiphenylarsenious chloride dihydrochloride (X), which was obtained in a crystalline condition.


(IX.)   (X.)
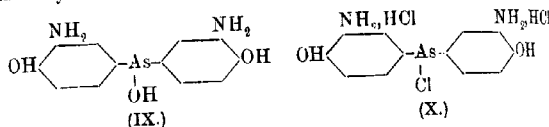
If the acid is first reduced to the corresponding *amino-acid* by means of sodium hyposulphite and then completely reduced by means of hypophosphorous acid, 3:3':3'':3'''-tetra-amino-4:4':4'':4'''-tetrahydroxytetraphenyldiarsine (XI) is obtained.

The degree of reduction of the products is readily ascertained by titration with a standard solution of iodine, using starch as indicator, oxidation to the corresponding arsinic acids taking place (compare Gaebel, *Arch. Pharm.*, 1911, **249**, 241).


(XI.)   (XII.)
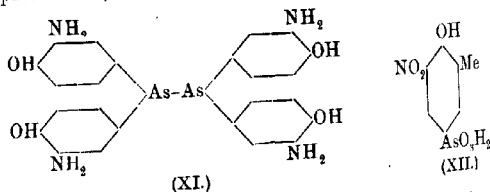
5-Nitro-6-hydroxy-*m*-tolylarsinic acid (XII), first obtained by Benda and Bertheim (*loc. cit.*) by the nitration of 4-hydroxy-*m*-

tolylarsinic acid, can also be prepared from 4-*oxalylamino-m-tolyl-
arsinic acid* by the series of reactions outlined above, the prepara-
tions from both sources being identical. On reduction with sodium
hyposulphite, diaminoarseno-*o*-cresol (4 : 4'-dihydroxy-5 : 5'-diamino-
3 : 3'-dimethylarsenobenzene) (XIII) (D.R.-P. 224953) was obtained.
This was converted into the *dihydrochloride*, which closely resembles
salvarsan (XIV).

OH   OH   OH   OH

NH₂ ⟨ ⟩ Me   Me ⟨ ⟩ NH₂   HCl,NH₂ ⟨ ⟩   ⟨ ⟩ NH₂,HCl

As═════As   As═══As
(XIII.)   (XIV.)
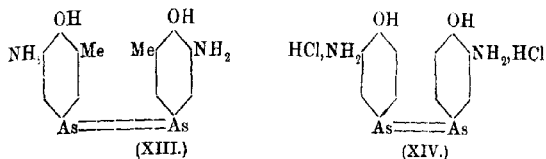
By the action of carbonyl chloride on *o*-aminophenol, 1 : 2-di-
hydrobenzoxazolone (XV) is obtained (Schmitt and Henschel, *J.
pr. Chem.*, 1888, [ii], **37**, 27; E. von Meyer, *ibid.*, 1915, [ii], **92**,
255). This reaction was applied to 3-amino-4-hydroxyphenylarsinic
acid (XVI), giving 1 : 2-*dihydrobenzoxazolone-4-arsinic acid*
(XVII), which, on reduction with sodium hyposulphite, yielded
the corresponding *arsenobenzene*. It had been hoped that this
would prove sufficiently acidic to dissolve in sodium carbonate, but
although it dissolves very readily in sodium hydroxide, it is prac-
tically insoluble in the carbonate.

O—CO   OH   O—CO

⟨ ⟩ NH   ⟨ ⟩ NH₂   ⟨ ⟩ NH

              AsO₃H₂   AsO₃H₂
(XV.)   (XVI.)   (XVII.)
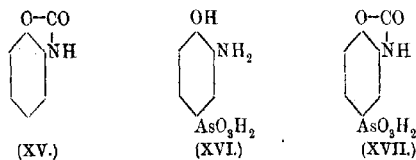
The estimation of arsenic in organic compounds has been the
subject of a recent communication by Ewins (T., 1916, **109**, 1355),
who considers that the method devised by Lehmann (*Apoth. Zeit.*,
1912, **27**, 545) for the estimation of arsenic in salvarsan and neo-
salvarsan, whilst applicable to certain closely allied derivatives,
fails entirely in a large number of cases owing to the fact that the
preliminary treatment with potassium permanganate and sulphuric
acid does not bring about complete oxidation. By a slight alter-
ation of the conditions, it has now been found possible to extend
this estimation to a considerable number of substituted phenyl-
arsinic acids containing nitro-, amino-, hydroxy-, methoxy-, bromo-,
and other groups, which, by the unmodified method, gave very
untrustworthy results owing to incomplete oxidation.

Experimental.

pp'-*Dihydroxydiphenylarsinic Acid* (III).

pp'-Dihydroxydiphenylarsinic acid was obtained by Benda (*Ber.*, 1908, **41**, 2371) by diazotising pp'-diaminodiphenylarsinic acid in dilute hydrochloric or sulphuric acid, and decomposing the diazo-derivative by passing steam through the solution. Diazotisation in hydrochloric acid, however, gives a product substituted to some extent by chlorine, whilst in sulphuric acid alone the product is very dark-coloured and difficult to purify.

10·5 Grams of sodium pp'-diaminodiphenylarsinate, containing $6H_2O$, were dissolved in 75 c.c. of water, 10 c.c. of sulphuric acid added, and diazotised with 50 c.c. of a normal solution of sodium nitrite. The product was mixed with an equal volume of acetic acid to keep the hydroxy-acid produced in solution, and warmed on the water-bath until the elimination of nitrogen had ceased. After boiling with charcoal, the solution was concentrated under diminished pressure, when, on cooling, rather more than 5 grams of the hydroxy-acid separated, whilst the mother liquors yielded further small quantities, the total yield amounting to 75—80 per cent. of the theoretical. The acid is very sparingly soluble in acetone or chloroform, but readily so in methyl alcohol, ethyl alcohol, or 50 per cent. acetic acid, from which it crystallises in plates melting and decomposing at 259° (corr.). (Found: $C = 49·0$; $H = 3·7$; $As = 25·3$.　$C_{12}H_{11}O_4As$ requires $C = 49·0$; $H = 3·8$; $As = 25·5$ per cent.)

$3 : 3'$-*Dinitro*-4 : 4'-*dihydroxydiphenylarsinic Acid* (IV).

6·3 Grams of pp'-dihydroxydiphenylarsinic acid were dissolved in 35 c.c. of concentrated sulphuric acid and treated gradually with a mixture of 2·5 c.c. of nitric acid (D 1·44) and 2·5 c.c. of sulphuric acid, the temperature being kept at $-5°$ to $-3°$. After the mixture had remained in a cool place for some time, it was poured on 250 grams of powdered ice, the precipitated acid being collected and washed with water. The yield amounted to 94 per cent. of the theoretical. The acid is almost insoluble in boiling water, fairly readily soluble in glacial acetic acid, and sparingly so in 50 per cent. acetic acid, from which it separates in minute, rhomboidal prisms melting and decomposing at 230° (corr.).

Found: $C = 37·5$; $H = 2·6$; $N = 7·3$; $As = 19·6$.
$C_{12}H_9O_8N_2As$ (384·1) requires $C = 37·5$; $H = 2·4$; $N = 7·3$; $As = 19·5$ per cent.

$3 : 3'$-*Diamino*-4 : 4'-*dihydroxydiphenylarsenious Chloride Dihydrochloride* (X).

Two grams of the preceding compound, dissolved in 20 c.c. of water and $5\cdot4$ c.c. of $2N$-sodium hydroxide, were added to a solution of 6 grams of magnesium chloride and 24 grams of sodium hyposulphite in 200 c.c. of water. The resulting solution, which immediately decolorised, was heated to $60°$ in an atmosphere of carbon dioxide for an hour, a further 10 grams of sodium hyposulphite being added after half an hour. The small quantity of grey powder obtained was dissolved in a little methyl alcohol containing hydrochloric acid, filtered, and added to 100 c.c. of concentrated hydrochloric acid, when a crystalline precipitate gradually separated. This was collected, washed with a few drops of glacial acetic acid and a little ether, and dried in a vacuum over sulphuric acid, the yield amounting to $0\cdot5$ gram.

The compound forms glistening leaflets readily soluble in water or methyl alcohol, but sparingly so in concentrated hydrochloric acid. On heating, it darkens above $170°$ and melts at $215°$ (corr.).

Found: $C = 36\cdot2$; $H = 3\cdot8$; $N = 6\cdot9$; $Cl = 27\cdot0$.

$C_{12}H_{13}O_2N_2ClAs,2HCl$ $(399\cdot5)$ requires $C = 36\cdot0$; $H = 3\cdot5$; $N = 7\cdot0$; $Cl = 26\cdot7$ per cent.

$0\cdot1000$ Gram required $0\cdot061$ gram of iodine for complete oxidation, against $0\cdot063$ theoretically required.

$3 : 3'$ - *Diamino* - 4 : 4' - *dihydroxydiphenylarsinic Acid and* $3 : 3' : 3'' : 3'''$-*Tetra-amino*-4 : 4' : 4'' : 4'''-*tetrahydroxytetra-phenyldiarsine Tetrahydrochloride.*

$5\cdot1$ Grams of $3 : 3'$-dinitro-4 : 4'-dihydroxydiphenylarsinic acid were dissolved in 80 c.c. of water and 24 c.c. of $2N$-sodium hydroxide. The solution, cooled to $0°$, was treated in one operation with $17\cdot6$ grams of commercial sodium hyposulphite, the temperature rising to about $30°$. When the reaction was complete, the solution was cooled, 20 c.c. of $2N$-hydrochloric acid were added, and as the acid only partly separated, it was salted out by the addition of sodium chloride, and was obtained as a sandy, crystalline precipitate fairly readily soluble in water or methyl alcohol, but sparingly so in ethyl acetate. The yield amounted to 46 per cent. of the theoretical. (Found: $N = 8\cdot5$. $C_{12}H_{13}O_4N_2As$ $(324\cdot1)$ requires $N = 8\cdot6$ per cent.)

Two grams of the acid were heated at $60°$ for one hour in an atmosphere of carbon dioxide with 20 c.c. of hypophosphorous acid

(D 1·15) and a trace of hydriodic acid. As the colourless base obtained by neutralising a test portion of the resulting solution rapidly became purple on exposure, the remainder was added without neutralisation to 150 c.c. of hydrochloric acid. The white precipitate which gradually separated was collected, washed with a few drops of glacial acetic acid and a little dry ether, and dried in a vacuum. The product is readily soluble in water or methyl alcohol.

Found: $N = 7·6$; $Cl = 19·7$.

$C_{24}H_{24}O_4N_4As_2,4HCl$ (728·1) requires $N = 7·7$; $Cl = 19·5$ per cent.

0·1001 Gram required 0·103 gram of iodine for complete oxidation, as against 0·104 gram theoretically required.

pp′-Dioxalylaminodiphenylarsinic Acid (V).

When oxalic acid is allowed to react with $pp′$-diaminodiphenylarsinic acid at a temperature approaching 160°, some fission of the molecule results, so that a mixture is obtained from which the desired product can be isolated by taking advantage of the sparing solubility of its barium salt in cold dilute ammonia, the barium salt of p-aminophenylarsinic acid being precipitated only on boiling.

8·4 Grams of sodium $pp′$-diaminodiphenylarsinate containing $6H_2O$ were intimately mixed with 15·1 grams of oxalic acid and heated in an oil-bath with constant stirring at 140° until most of the water had disappeared, and then to 160° until quite hard. The product was well ground with 80 c.c. of water and 8 c.c. of hydrochloric acid, collected, and well washed with water. It was then dissolved in ammonia and treated with a cold solution of barium chloride. The resulting precipitate was collected, well washed with water, and decomposed by grinding with dilute hydrochloric acid. A small quantity which remained in the acid was precipitated on dilution. pp′-Dioxalylaminodiphenylarsinic acid is only sparingly soluble in boiling water, alcohol, or methyl alcohol, and practically insoluble in benzene, ether, or ethyl acetate. It is more readily soluble in acetic acid or 50 per cent. acetic acid, and crystallises in slender needles which contain $4H_2O$.

Found: loss at $110° = 13·8$.

$C_{16}H_{13}O_6N_2As,4H_2O$ requires 14·1 per cent.

In material dried at 110°, $C = 44·1$; $H = 3·3$; $N = 6·4$.

$C_{16}H_{13}O_6N_2As$ (436·2) requires $C = 44·0$; $H = 3·0$; $N = 6·4$ per cent.

Nitration with a mixture of nitric and sulphuric acids, and subsequent acid hydrolysis, led to the formation of 3:3′-dinitro-4:4′-

diaminodiphenylarsinic acid (VI), a yellow, crystalline powder very sparingly soluble in water and the usual organic solvents.

Found: $N = 14.3$.

$C_{12}H_{11}O_6N_4As$ (382.1) requires $N = 14.7$ per cent.

This was converted by warming with an excess of potassium hydroxide solution into $3:3'$-dinitro-$4:4'$-dihydroxydiphenylarsinic acid, identical with that described above.

6-*Oxalylamino*-m-*tolylarsinic Acid*.

Five grams of sodium 6-amino-*m*-tolylarsinate (containing $3H_2O$) and 6 grams of oxalic acid were intimately mixed and heated first at 140° until most of the water had been driven off, and then at 160° until quite dry. The residue was triturated with 50 c.c. of water and 7 c.c. of hydrochloric acid, collected, and washed with water. The product, which was anhydrous, amounted to rather more than 3 grams. It was found to be sparingly soluble in hot alcohol, ethyl acetate, or acetone, more readily so in hot water, and readily so in 50 per cent. acetic acid, from which it crystallised in elongated, rhombic prisms.

Found: $N = 4.5$; $As = 24.6$.

$C_9H_{10}O_6NAs$ (303.1) requires $N = 4.6$; $As = 24.7$ per cent.

5-*Nitro*-6-*amino*-m-*tolylarsinic Acid*.

Six grams of the above oxalyl derivative were dissolved in 20 c.c. of sulphuric acid, and a mixture of 1.2 c.c. of nitric acid (D 1.4) and 1.2 c.c. of sulphuric acid was gradually added below 15°. When the reaction was complete, the product was poured into 100 c.c. of water, boiled under a reflux condenser for two hours, cooled, and the acid which separated, amounting to 4.6 grams, collected. 5-*Nitro*-6-*amino*-m-*tolylarsinic acid* is fairly readily soluble in boiling water, from which it separates in slender needles consisting of a mixture of the yellow anhydrous form and the orange hydrated form. It gradually passes completely into the latter, which contains $1\frac{1}{2}H_2O$.

Found: loss at 110° = 9.3.

$C_7H_9O_5N_2As, 1\frac{1}{2}H_2O$ requires $H_2O = 9.0$ per cent.

In dried substance, $N = 9.9$.

$C_7H_9O_5N_2As$ (276.1) requires $N = 10.1$ per cent.

*5-Nitro-6-hydroxy-*m-*tolylarsinic Acid* (XII).

Two grams of the acid just described were heated on the water-bath with 10 c.c. of 40 per cent. potassium hydroxide solution until a test portion no longer showed the presence of an amino-group. The product was then cooled and acidified with hydrochloric acid, giving almost the theoretical yield of 5-nitro-6-hydroxy-*m*-tolylarsinic acid. This was compared with a specimen prepared by Benda and Bertheim's method (*Ber.*, 1911, **44**, 3445), and found to be identical with it. Both products, when crystallised rapidly from boiling water, formed clusters of slender, yellow needles, and when crystallised slowly from 50 per cent. acetic acid, well-defined, rhombic prisms. When heated in the same bath, both products decomposed explosively at 310°, whilst the mixture of the two behaved identically.

The *acetyl* derivative, prepared by the action of acetic anhydride in the presence of a trace of pyridine, is fairly readily soluble in methyl or ethyl alcohol or boiling water, but sparingly so in cold water or ethyl acetate. When crystallised from water, it forms colourless, spherical nodules, which are anhydrous.

Found: $N = 4.4$.
$C_9H_{10}O_7NAs$ (319.1) requires $N = 4.4$ per cent.

4 : 4′-Dihydroxy-5 : 5′-diamino-3 : 3′-dimethylarsenobenzene Dihydrochloride.

The reduction of the 5-nitro-6-hydroxy-*m*-tolylarsinic acid was effected by means of sodium hyposulphite under the conditions described by Ehrlich and Bertheim (*Ber.*, 1912, **45**, 757; compare D.R.-P. 224953). The dihydrochloride, which was obtained in a yield of 70 per cent. of the theoretical, formed a pale yellow, microcrystalline powder readily soluble in water or methyl alcohol, much less readily so in ethyl alcohol, and practically insoluble in ether or acetone.

Found: $Cl = 13.6$; $As = 29.9$.
$C_{14}H_{16}O_2N_2As_2,2HCl,2H_2O$ (503.1) requires $Cl = 14.1$; $As = 29.8$ per cent.

3-Amino-4-hydroxyphenylarsinic Acid.

The reduction of nitrohydroxyphenylarsinic acid to the corresponding amino-acid by means of sodium hyposulphite has been

described in D.R.-P. 224953. The following modification of the method gives excellent results.

Twenty-six grams of 3-nitro-4-hydroxyphenylarsinic acid were dissolved in 200 c.c. of N-sodium hydroxide, cooled to $-2°$, and to the well-stirred solution 65 grams of sodium hyposulphite (80 per cent.) were added in one operation. The colour of the solution disappeared at once, and the temperature rose to 25°, whilst the amino-acid commenced to deposit. The precipitation was completed by the addition of 23 c.c. of hydrochloric acid (D 1·12). The acid was collected and well washed with water; the yield in several experiments ranged between 65 and 80 per cent. of the theoretical.

1 : 2-Dihydrobenzoxazolone-4-arsinic Acid (XVII).

A solution of 11·6 grams of aminohydroxyphenylarsinic acid in 150 c.c. of 5 per cent. sodium hydroxide, cooled by ice and stirred vigorously, was gradually treated with 110 c.c. of a 6·5 per cent. solution of carbonyl chloride in toluene. At the conclusion of the reaction, the two layers were separated, the aqueous layer being extracted with ether and then acidified with hydrochloric acid, when the oxazolone separated as a sandy, crystalline precipitate in a yield amounting to 83 per cent. of the theoretical.

It is sparingly soluble in alcohol, but readily so in boiling water, from which it separates in colourless, prismatic needles which are anhydrous. On heating, it rapidly decomposes above 250° without melting.

Found: $C = 32·5$; $H = 2·5$; $N = 5·4$; $As = 28·6$.
$C_7H_6O_5NAs$ (259·0) requires $C = 32·4$; $H = 2·3$; $N = 5·4$; $As = 28·9$ per cent.

1 : 2 : 1' : 2'-Tetrahydro-4-arsenobenzodioxazolone.

2·3 Grams of 1 : 2-dihydrobenzoxazolone-4-arsinic acid were dissolved in a mixture of 50 c.c. of water and 8 c.c. of 2N-sodium hydroxide, added to a solution of 15 grams of sodium hyposulphite and 3 grams of magnesium chloride in 70 c.c. of water, and heated, with stirring, for an hour at 60° in an atmosphere of carbon dioxide. A yellow, granular precipitate gradually formed, which, after cooling, was collected and well washed with water. A portion was dried to constant weight in a vacuum over sulphuric acid, and formed a pale yellow, granular powder insoluble in water or the usual organic solvents or in sodium carbonate, but readily soluble in aqueous sodium hydroxide.

Found: N = 6·5 ; As = 35·6.

$C_{14}H_8O_4N_2As_2$ (418·1) requires N = 6·7 ; As = 35·9 per cent.

The remainder was dissolved in aqueous sodium hydroxide, and the *sodium* salt precipitated by the addition of alcohol. This, after drying in a vacuum, was obtained as a pale yellow, fairly stable powder readily soluble in water, sparingly so in alcohol, and insoluble in ether.

Estimation of Arsenic in Substituted Phenylarsinic Acids.

For the estimation of arsenic in the foregoing and many other compounds, the following modification of Lehmann's method (*Apoth. Zeit.*, 1912, **27**, 545) has been used, and has been found to give good results generally with substituted phenylarsinic acids.

0·2 Gram of the powdered substance is accurately weighed and intimately mixed in a 250 c.c. flask with 1 gram of potassium permanganate. Five c.c. of 50 per cent. sulphuric acid are added, followed by a further 10 c.c. of concentrated sulphuric acid when the first reaction has ended. After a few minutes, 10 c.c. of water are added, and the mixture is heated for half an hour to gentle boiling, precautions being taken against loss by spraying. The manganese dioxide is then removed by a slight excess of hydrogen peroxide, 30 c.c. of water are added, and the solution is again boiled for ten minutes, after which a dilute solution of potassium permanganate is added drop by drop until a faint, permanent pink tinge is obtained. This is discharged by the addition of a drop of a dilute solution of oxalic acid. The solution is then cooled. 2·5 grams of potassium iodide are added, the whole being allowed to remain for an hour, and the liberated iodine titrated by means of thiosulphate. A blank experiment should be carried out alongside each estimation, and the final reading corrected accordingly.

The following are examples of the results obtained :

Substance.	As Found.	Calc.
3-Nitro-4-hydroxyphenylarsinic acid......................	28·4, 28·4	28·5
p-Aminophenylarsinic acid	34·5, 34·5	34·6
1 : 2-Dihydrobenzoxazolone-4-arsinic acid	28·6	28·9
3-Nitro-4-aminophenylarsinic acid........................	28·9, 28·8	28·6
3 : 3′-Dinitro-4 : 4′-dihydroxydiphenylarsinic acid......	19·6, 19·5	19·5
p-Bromophenylarsinic acid	26·5	26·7

In conclusion, the author desires to express his thanks to Professor F. L. Pyman for his interest during the course of the investigation.

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LXXXIV.—*The Selective Combustion of Carbon Monoxide in Hydrogen.*

By ERIC KEIGHTLEY RIDEAL.

IN a recent communication (*Analyst*, 1919, **44**, 89), it was shown that small quantities of carbon monoxide in hydrogen could be preferentially oxidised to carbon dioxide by passing the gaseous mixture admixed with a small quantity of oxygen over certain catalytic materials maintained at suitable temperatures.

The following conclusions were drawn, namely, that the preferential nature of the combustion was affected by the nature and temperature of the catalyst employed; thus, the oxides of copper (operative at 110°) and of iron and chromium (operative at 250° to 350°) were extremely efficacious in inducing the combustion of the carbon monoxide, whilst an enhanced activity could be obtained by the addition of certain promoters, such as ceria and thoria, in small quantities to the mixed oxides. With reduced nickel, on the other hand, complete interaction of oxygen and the hydrogen was obtained. At the time, it was considered probable that with suitable catalytic material maintained at the proper temperatures only carbon monoxide, and no hydrogen, could be burnt, the selective nature of the reaction being gradually lost with elevation of the temperature. It was also established that complete elimination of the carbon monoxide could be effected by this means, and that the mechanism was not founded on the operation of the water-gas reaction, $H_2O + CO \rightleftharpoons H_2 + CO_2$, at low temperatures.

In view of the importance of the processes of selective combustion, such as of hydrogen sulphide in hydrogen, phosphine in ammonia, which are being investigated, and of the present example, it was deemed of interest to study the mechanism of the reaction in somewhat greater detail in order, if possible, to obtain material to assist in making a decision as to the validity of the various theories of heterogeneous catalysis which are now extant. In the case of the catalytic combination of hydrogen and oxygen on the surface of platinum black, the theory of an intermediate compound is strongly supported by the work of Engler and Wöhler (*Zeitsch. anorg. Chem.*, 1901, **29**, 1; *Ber.*, 1903, **36**, 2642), whilst Sabatier, in his researches on hydrogenation by means of metallic nickel, concluded that his results were explicable on the assumption that an unstable nickel hydride was formed ("La Catalyse en Chimie Organique").

Faraday (*Phil. Trans.*, 1834, **114**, 55), on the other hand, gave ardent support to the adsorption theory.   Recently, Bancroft (*J. Physical Chem.*, 1917, **21**, 8), from a survey of the work of Turner, Henry, Lunge, Harbeck, and Bone, draws the conclusion that the facts are capable of the simplest explanation on the adsorption theory.

The adsorption theory, however, is capable of several interpretations, which at the present time are developing along two distinct lines, that may be termed the *diffusion theory* and the *single layer theory*.   In the diffusion theory, which finds its expression in the work of Bodenstein (*Zeitsch. physikal. Chem.*, 1899, **29**, 655, *et seq.*), and for which some support can be gained from the experiments of Bone and his co-workers (*Phil. Trans.*, 1906, [*A*], **206**, 1), the adsorbed layer is relatively thick and the velocity of reaction is governed rather by the rate of diffusion of the reactants and products in this layer than by the rate of chemical change occurring at the actual surface of the catalyst.   In the single layer theory, advanced by Langmuir (*J. Amer. Chem. Soc.*, 1916, **38**, 2221; 1917, **39**, 1848; 1918, **40**, 1361), Harkins (*ibid.*, 1917, **39**, 591), and Marcelin, the surface film is considered to be only one molecule thick, thus showing an abrupt change in continuity, and the reactions take place in that surface skin.   Lewis (this vol., p. 182) has recently applied the radiation hypothesis to explain the enhanced reaction velocities obtained in the presence of heterogeneous catalytic materials, and has adopted the "single layer" theory as "the most probable material mechanism of the process considered."   A summary of the results of Bodenstein and Bone and Wheeler on the catalytic combination of hydrogen and oxygen is likewise given in this paper.   Bodenstein and Ohmer's investigations (*Zeitsch. physikal. Chem.*, 1905, **53**, 166) on the catalytic combination of carbon monoxide and oxygen on the surface of hot quartz between 300° and 570° led them to the conclusion that the rate of combination was proportional to the partial pressure of the oxygen and inversely proportional to the concentration of carbon monoxide, a case of negative catalysis; estimations were carried out by the manometric method.

EXPERIMENTAL.

The catalytic materials investigated were prepared as follows:

Iron oxide, prepared by the gentle ignition of the nitrate, the remainder of the oxides of nitrogen being expelled by heating in a current of steam at 400°.   The coarse lumps obtained in this way were broken up, and uniform pieces, some 0·2 cm. in diameter, utilised for experimental purposes.

Iron oxide containing 2·5 per cent. of chromium oxide and 0·5 per cent. of cerium oxide, prepared in a similar manner from the nitrates of iron and cerium with the admixture of the chromium salt in the form of ammonium dichromate.

Copper oxide prepared from copper wire by alternate oxidation and reduction with air and hydrogen respectively. The gases were carefully freed from any possible contamination with hydrogen sulphide or sulphur dioxide. The copper oxide was considered sufficiently active when appreciable quantities of water were formed when hydrogen was passed over it at 120°.

Nickel prepared by soaking small pieces of diatomite in nickel nitrate, followed by gentle ignition and heating in superheated steam. The finished product contained 5 per cent. of nickel.

Palladium.—An ordinary purchased sample of good quality palladised asbestos was used for this purpose.

Preliminary experiments having shown that it was extremely difficult to prepare two specimens of catalytic material identical in activity, and, further, that the activity of the catalyst underwent marked fluctuations in the course of an experiment, first increasing and then decreasing, it was decided not to attempt to measure the relative velocities of catalytic combustion of hydrogen and carbon monoxide in separate experiments, but to determine the relative rates of combustion of these constituents in gas mixtures containing hydrogen, oxygen, and carbon monoxide.

The gas mixtures of various compositions were obtained from electrolytic hydrogen and oxygen and carbon monoxide produced from oxalic and sulphuric acids, the carbon dioxide being removed by means of sodium hydroxide. Prior to use, the gas mixture was carefully freed from any traces of carbon dioxide and from moisture by means of soda-lime and phosphoric oxide.

The furnace was similar to that employed in the analytical instrument previously mentioned, but was constructed throughout of silica instead of glass. It consisted essentially of two co-axial silica tubes, the outer one electrically heated and so arranged that the gases could pass in through the annular space between the tubes and down through the catalyst in the central tube. In this way, uniformity of temperature in the catalyst was ensured.

In each experiment, 5 c.c. of catalyst were employed; no attempt was made to approximate to the same superficial area of catalytic material, although experiments have shown that with a uniform catalytic material the activity is proportional to the superficial area of the grains; this generalisation, however, does not apply to fine powders or to relatively large pieces of porous materials.

A series of experiments was conducted by passing the gas mixture through the catalytic material maintained at suitable tempera-

tures, and determining the quantities of water and carbon dioxide formed by the usual methods adopted in processes of organic combustion, namely, absorption and weighing. In all cases, the temperature was accurately controlled by means of a thermometer, around the bulb of which the catalytic material was built up, and care was taken to ensure passage of the gas mixture through the furnace at such a rate that the fractional conversion was but small. This consideration is of some importance in the light of the diffusion theory, for if we imagine the surface of the catalyst to be covered with a small atmosphere of the products of the reaction, carbon dioxide and steam, then, if the gas is quiescent, fresh reactants can only approach the catalyst by diffusion, and the atmosphere will slowly extend from the surface of the catalyst to the walls of the containing vessel. Under these conditions, the phenomenon of catalysis is not being observed, but there are recorded merely some rates of diffusion liable to large errors caused by convection, especially if the reaction is strongly exothermic. A gentle movement of the gas will consequently upset these conditions, and the rates of reaction will be affected by the nature and magnitude of this movement.

This does not necessarily preclude the diffusion theory of cata-lysis, since in this case it is assumed that the atmosphere round the catalyst is maintained by the molecular forces of the material, and that the "diffusion layer," as in the case of liquid and solid surfaces investigated by Noyes and Whitney (*Zeitsch. physikal. Chem.*, 1897, **23**, 689), is relatively thin—of the order of 0·05 to 0·1 mm. It will therefore suffice always to maintain the gas velocity past the catalyst grains, so that the "diffusion layer," if it exists at all, will not exceed the normal thickness produced by adsorption. On the other hand, the velocity of the flow of gas must not be raised too high, since evidence is not lacking in the possibly analogous case of liquid and solid surfaces that the adsorption film is affected by high velocities; thus, A. Fischer and the author computed that the thickness of the film was reduced from 0·0635 mm. to 0·0510 mm. by agitating the liquid by means of a stirrer rotating at 250 and 1100 revolutions per minute respectively.

In the first series of experiments, a mixture containing approximately 10 per cent. of carbon monoxide, 10 per cent. of oxygen, and 80 per cent. of hydrogen was passed through the various catalytic materials at various temperatures from 150° to 380°. Below 150°, the activity of all the catalysts employed, with the exception of palladium, was too slight to yield trustworthy results, and at high temperatures the activity became so great that, in spite of reducing

the quantity of catalyst in the furnace and considerably augment-
ing the velocity of the gas, a very considerable conversion of the
reactants took place, which, for the reasons already stated, was
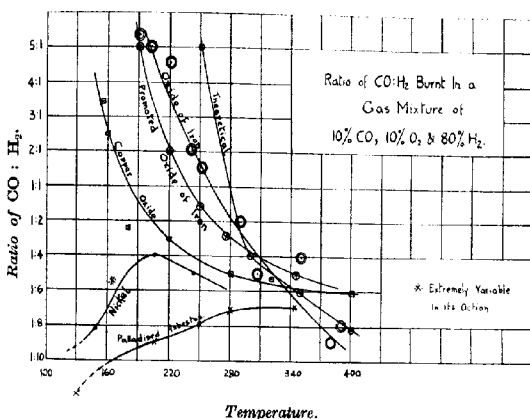undesirable.

The results of these experiments are shown in the attached
curves, from which the two following typical examples may be
cited:

Catalyst, iron oxide.

Temperature, 220°.

Composition of gas: $CO = 9$; $O_2 = 14$; $H_2 = 77$ per cent.

Vol. of gas used. Litres.	Time in hours.	Weight of H_2O collected.	Weight of CO_2 collected.	Ratio vol. $CO : H_2$ burnt.
0·768	1·5	0·0121	0·1332	4·43 : 1
0·568	1·75	0·0092	0·0964	4·22 : 1
0·424	2·0	0·0062	0·0702	4·28 : 1
			Mean.........	4·32 : 1

Ratio of $CO:H_2$ Burnt in a Gas Mixture of 10% CO, 10% O_2, & 80% H_2.

* Extremely Variable in its Action

Temperature.

Catalyst, copper oxide.

Temperature, 280°.

Composition of gas: $CO = 14$; $O_2 = 11·5$; $H_2 = 74·5$ per cent.

Vol. of gas used. Litres.	Time in hours.	Weight of H_2O collected.	Weight of CO_2 collected.	Ratio vol. $CO : H_2$ burnt.
1	0·5	0·0442	0·0508	0·470 : 1
1	0·5	0·0298	0·0344	0·472 : 1
1	0·5	0·0390	0·0431	0·452 : 1
			Mean.........	0·466 : 1

In all cases, the interesting observation was made that a catalyst which had been allowed to cool exposed to the air, liberated first, on warming in the stream of gas, a relatively large quantity of carbon dioxide, and, at higher temperatures, water vapour; further, on raising the temperature of a catalyst in the mixture of gases, the ratio $CO : H_2$ burnt, as obtained by estimation of the water and carbon dioxide, during the first twenty minutes or so, fell short of the ratio when constant velocity ratios were obtained.

In the second series of experiments, only one catalytic material was employed, namely, iron oxide, and the gaseous mixture was altered in composition in order to determine the effect of an alteration in the partial pressures of the reactants on the relative rates of reaction.

In these experiments, the temperature of the catalyst was maintained at 220°, when the following ratios were obtained:

	Composition of gas per cent.			Ratio $CO : H_2$ by volume burnt. Mean of several experiments.
Expt. No.	CO.	O_2.	H_2	
1	12·3	10·0	77·7	1·24 : 1
2	4·6	5·1	90·3	0·54 : 1
3	2·3	5·5	42·7	0·21 : 1
4	5·7	7·0	88·3	0·52 : 1
5	2·5	39·0	48·5	0·30 : 1
6	12·0	12·6	75·4	1·25 : 1
7	16·6	19·2	64·2	1·6 : 1

Discussion of Results.

It will be noticed from the curves that in no case is the selective combustion of carbon monoxide in hydrogen perfectly complete; in all cases we are dealing with two simultaneous reactions, the oxidation of hydrogen and of carbon monoxide, the velocity of each naturally varying with the temperature, the composition of the gas, and also with the nature of the catalytic material employed.

The results do not appear compatible with the theory of an intermediate compound as interpreted in the older sense and not on Langmuir's view of surface combination, since no evidence of stable hydrides or carbonyls was obtained. The results, in addition, do not favour the adsorption theory of catalysis, for the following reasons.

Assuming that the reaction velocity is governed entirely by the rate of diffusion of the reactants through the atmosphere of carbon dioxide and steam around the material, then the relative reaction velocities, at any definite temperature, should not change to any marked extent with the nature of the catalytic material employed.

and, further, owing to the greater mobility of hydrogen, this gas should burn more quickly than carbon monoxide, especially at relatively low temperatures, when the adsorbed atmosphere is presumably denser than at more elevated temperatures. Neither of these deductions is confirmed by the experimental figures.

The general shape of the temperature:ratio curves obtained can, however, be deduced from theoretical considerations if Langmuir's theory of single layer absorption is adopted, together with Lewis's application of the Marcelin-Rice principle of activation to heterogeneous systems.

It is evident that the dependence of the ratio $CO:H_2$ burnt, on the partial pressure of the reactants on a given catalyst at a definite temperature, indicates the relative reaction velocities of two separate reactions, the surface oxidation of hydrogen and of carbon monoxide; these can be expressed in the form:

I $\quad$ (a) $2H_2 + O_2 \longrightarrow 2H_2O$

$\quad\quad$ (b) $H_2 + O_2 \longrightarrow H_2O_2 \longrightarrow H_2O$

II $\quad$ (a) $2CO + O_2 \longrightarrow 2CO_2$

$\quad\quad$ (b) $CO + O_2 \longrightarrow CO_3 \longrightarrow CO_2$

$\quad\quad$ (c) $CO + \frac{1}{2}O_2 \longrightarrow CO_2$
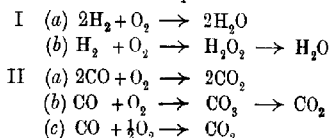
Lewis gives evidence in favour of assuming that in the case of the combustion of hydrogen the primary reaction is

$$H_2 + O_2 \longrightarrow H_2O_2,$$
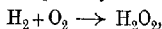
supported to some extent by the work of Bone and Wheeler (*Phil. Trans.*, 1906, [*A*], **206**, 1), who disagree with Bodenstein (*Zeitsch. physikal. Chem.*, 1899, **29**, 665), whose figures for the velocity constant corresponded with the reaction

$$2H_2 + O_2 = 2H_2O.$$
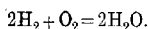
In the present instance, where ratios alone are being considered, we can easily distinguish between these reactions, since if each reaction follows the same course, for example. I (a) and II (a), then, since
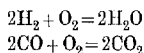
$$2H_2 + O_2 = 2H_2O$$
$$2CO + O_2 = 2CO_2$$
$$-\frac{dc_{H_2}}{dt} = (H_2)^2(O_2)$$

and

$$-\frac{dc_{CO}}{dt} = (CO)^2(O_2)$$

or

$$\frac{-\dfrac{dc_{CO}}{dt}}{-\dfrac{dc_{H_2}}{dt}} = \frac{(CO)^2}{(H_2)^2},$$

that is, the relative velocities of combustion are independent of the concentration of oxygen.

If, on the other hand, the oxidation of hydrogen and carbon monoxide proceeds differently, say according to the equations I (b) and II (c), then, since

$$H_2 + O_2 \longrightarrow H_2O_2 \longrightarrow H_2O$$
$$CO + \tfrac{1}{2}O_2 \longrightarrow CO$$
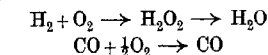
$$\dfrac{-\dfrac{dc_{CO}}{dt}}{-\dfrac{dc_{H_2}}{dt}} = \dfrac{(CO)(O_2)^{\frac{1}{4}}}{(H_2)(O_2)} = \dfrac{(CO)}{(H_2)(O_2)^{\frac{1}{4}}},$$

that is, the relative rates will be a function of the pressure of oxygen. From the above experimental determinations, all the possible ratios can be calculated. A few trials were sufficient to indicate that one ratio, and one ratio only, gave figures closely approximating to those experimentally determined, namely,

$$\dfrac{-\dfrac{dc_{CO}}{dt}}{-\dfrac{dc_{H_2}}{dt}} = \dfrac{(CO)}{(H_2)(O_2)^{\frac{1}{4}}}$$

and the experimental and calculated values are given in the following table:

Expt. No.	Ratio: $\dfrac{CO : H_2 \text{ (Expt. I.)}}{CO : H_2 \text{ (Expt. II.)}}$ of gases burnt.	Ratio: $\dfrac{\frac{(CO)}{(H_2)(O_2)^{\frac{1}{4}}} \text{ (Expt. I.)}}{\frac{(H_2)(O_2)^{\frac{1}{4}}}{CO} \text{ (Expt. II.)}}$ calculated from compositions of mixtures.
1		
2}	2·3	2·28
3}	2·6	3·0
4}	0·40	0·30
5}	1·7	2·9
6}	0·24	0·19
7}	0·77	0·76

It will be observed that, with the exception of the ratio expt. 4:5, the agreement is fairly good between the observed figures and those calculated on the assumption that the velocities of reaction are in accordance with one of the two following schemes:

$$A. \begin{cases} H_2 + O_2 \longrightarrow H_2O_2 \longrightarrow H_2O \\ CO + \tfrac{1}{2}(O_2) \longrightarrow CO_2 \end{cases}$$

$$B. \begin{cases} H_2 + \tfrac{1}{2}(O_2) \longrightarrow H_2O \\ CO \text{ rate independent of the concentration of oxygen.} \end{cases}$$
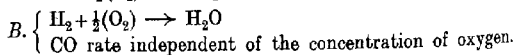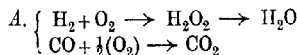
Although from these experiments it is impossible to distinguish between these two hypothetical cases, yet, in view of the fact that carbon monoxide is burnt on all the catalysts investigated, whether

oxides or not, it may be assumed that the first set of reactions is probably more correct, which on Langmuir's hypothesis would indicate that the hydrogen and carbon monoxide were bound by only one valency bond to the catalytic material, and the oxygen both by one and by two.

Lewis adopts the hypothesis that the oxygen is adsorbed by the catalyst and exists in the atomic state on its surface, and that all that is necessary is for an activated molecule of hydrogen or carbon monoxide to come into contact with an atom of oxygen. If we adopt the hypothesis that the number of active oxygen atoms or molecules are already present in large excess, and that the reaction velocity is governed entirely by the number of molecules of hydrogen or carbon monoxide that receive the necessary critical energy increment per second, then the ratio of gases burnt should be independent of the concentration of oxygen, which is not the case. It would appear, however, that the energy necessary to activate a gram-molecule of oxygen sufficiently for it to become reactive at the surface of such catalysts is extremely small, and for the purposes of calculation may be neglected.

The reaction velocity of each reaction is accordingly given by the expressions

$$-\frac{dc_{CO}}{dt} = ae^{-\frac{(Nhv_{CO} + L_{CO_2})}{RT}}$$

$$-\frac{dc_{H_2}}{dt} = a'e^{-\frac{(Nhv_{H_2} + L_{H_2O})}{RT}}$$

or

$$\frac{-\dfrac{dc_{CO}}{dt}}{-\dfrac{dc_{H_2}}{dt}} = \frac{a}{a'} e^{\frac{Nhv_H - Nhv_{CO} + L_{H_2O} - L_{CO_2}}{RT}}$$

where v_{CO}, v_{H_2} are the frequencies of the radiation bringing about the partial activation of hydrogen and carbon monoxide, N the number of molecules per gram-molecule, h Planck's constant, L_{H_2O} and L_{CO_2} the heat of desorption per gram-molecule of the products of the reaction, namely, water and carbon dioxide at the temperature T, $\frac{a}{a'}$ the ratio of the surface concentrations of carbon monoxide and hydrogen. For the purposes of calculation, L_{H_2O} and L_{CO_2} are taken as the latent heats of water and carbon dioxide at the respective temperatures, it being assumed that the values alter in a linear manner with the temperature. For water, the values adopted are 9000 calories at 100° and 0 at 365°, the critical

point; for carbon dioxide, 6200 calories at 0° and 0 at 35°. Lewis's value, deduced from Bohr's atomic model of 21,000 calories per gram-molecule, is taken as the experimental value of Nhv_a, whilst that for carbon monoxide was calculated as follows. Assuming the equality of the four carbon linkings in the carbon atom, then from the heats of combustion of carbon and its oxide:

$$C + O_2 = CO_2 + 94,320$$
$$CO + O = CO_2 + 68,220$$

Therefore $C + O = CO + 26,100,$
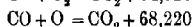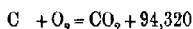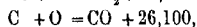
or the heat equivalent of two carbon–oxygen linkings is

$$68,220 - 26,100 = 42,120 \text{ calories,}$$

or 21,060 for one valency.

If we assume that the carbon monoxide is activated by desorption after adsorption on to the oxide catalyst by means of one carbon–oxygen valency, the necessary critical increment for such an activation is 21,060 calories per gram-molecule, or

$$Nhv_{CO} = 21,060.$$

Therefore $Nhv_{H_2} - Nhv_{CO} = -60$ calories only, or the spectral regions in which hydrogen and carbon monoxide are activated are practically identical. An approximately similar result may be obtained from the ionising potentials of the two gases. It can easily be shown that the critical increment Nhv is equal to $2\cdot2 \times 10^4 V$ (where V is the ionising potential in volts). The value of V for hydrogen is approximately 16 and for carbon monoxide about 15·8 to 15·9 volts; thus, in this case, $Nhv_{H_2} - Nhv_{CO} = +3000$ calories. These figures are necessarily somewhat inexact, and the degree of activation required for catalytic chemical reaction is probably much less than is required for ionisation, as indicated by the above figures.

The following table summarises the results of the calculation for the determination of the ratio of the reaction velocities at various temperatures, on the assumption that the activation of the oxygen is not a part of the process.

Temperature.	L_{H_2O}.	L_{CO_2}.	$\dfrac{-60 + L_{H_2O} - L_{CO_2}}{RT}$	$e^{\frac{-60 + L_{H_2O} - L_{CO_2}}{RT}}$
-50°	14,500	18,000	-9·0	0·0001
0	12,500	6,000	11·8	135,000
50	10,800	0	16·6	16×10^6
100	9,000	—	12·0	205,000
200	5,500	—	5·7	300
250	3,900	—	3·7	40·5
300	2,000	—	1·7	5·5
350	500	—	0·35	1·42
400	0	—	-0·04	0·96

The relative velocities of combustion for a mixture of carbon monoxide and hydrogen in the ratio of 1:8, calculated from the above table, are shown in the curve, and the similarity in form between this derived curve and that experimentally determined on the iron oxide catalyst is clearly indicated. A closer agreement is scarcely to be expected, since the factor introduced by the possible activation of the oxygen and the effect of its partial pressure on the reaction velocity have been neglected, together with the uncertainty introduced by equating the latent heat with the heat of desorption. It follows that the removal of carbon monoxide from hydrogen by this means takes place most readily at about 50° to 100°, whilst below −50° and above 400° hydrogen burns more quickly than carbon monoxide, selective combustion being entirely dependent on the fact that energy is required for the desorption of one of the products of combustion, namely, water vapour, although in the case of iron oxide it is scarcely sufficiently reactive below 220° to permit of the optimum conditions of operation.

It is interesting to note that at high temperatures hydrogen burns more quickly than carbon monoxide.

It is evident that the simple adsorption theory, where the hydrogen and carbon monoxide are adsorbed and activated by radiation and the oxygen is adsorbed and activated by the catalyst, gives an adequate explanation for the observed dependence of the reaction velocity ratios on the composition of the gas and on the influence of temperature, but these considerations do not give any insight into the dependence of the ratio on the composition of the catalyst.

The temperature-coefficients of both these reactions are sufficiently large to exclude the hypothesis that every hydrogen and carbon monoxide molecule striking the surface and becoming attached to the catalyst is oxidised; one is forced to assume that the ratio $\frac{a}{a}$, which is the ratio of the surface concentrations of the two gases, varies with the catalytic material. Adopting the hypothesis of molecular attachment by one bond for hydrogen and carbon monoxide, the ratio of the surface concentrations can be derived by Langmuir's equation:

$$\frac{N}{N_0} a = \frac{\sigma\mu}{1 + \sigma\mu}$$

where N = Avogadro's constant.

N_0 = number of space lattices per sq. cm.

$\sigma = \frac{A}{V}$, where V = rate of evaporation from a completely

covered surface; A, a factor approximating to unity, being the fraction of the number of molecules striking the surface which are absorbed.

$\mu =$ gram-molecules striking.

$= K\dfrac{P}{\sqrt{MT}}$, where P is the gas pressure, M the molecular weight, and T the absolute temperature.

$a =$ gram-molecules adsorbed per unit area.

Hence

$$\frac{a_{CO}}{a_{H_2}} = \frac{\sigma_1\mu_1(1+\sigma_2\mu_2)}{\sigma_2\mu_2(1+\sigma_1\mu_2)}$$

$$= \frac{P_{CO}A_{CO}(V_{H_2}\sqrt{M_{H_2}T}+A_{H_2}P_{H_2})}{P_{H_2}A_{H_2}(V_{CO}\sqrt{M_{CO}T}+A_{CO}P_{CO})}.$$

Putting $A_{CO}=A_{H_2}$,

$$\frac{a_{CO}}{a_{H_2}} = \frac{P_{CO}(V_{H_2}\sqrt{M_{H_2}T}+AP_{H_2})}{P_{H_2}(V_{CO}\sqrt{M_{CO}T}+AP_{CO})},$$

whilst if each molecule is attached by two bonds,

$$\frac{a_{CO}}{a_{H_2}} = \frac{\sqrt{\sigma_1\mu_1}}{\sqrt{\sigma_2\mu_2}} = \sqrt{\frac{V_{H_2}P_{CO}\sqrt{M_{H_2}}}{V_{CO}P_{H_2}\sqrt{M_{CO}}}}.$$

We have assumed in the former calculation that the surface concentration ratio $\dfrac{a}{a'}$ is equal to the ratio

$$K\,\frac{P_{CO}}{P_{H_2}}.\frac{V_{H_2}}{V_{CO}}$$

(where K is a constant), which is actually the case for any one particular catalytic material, but a closer approximation is given by

$$\frac{a}{a'} = K\frac{P_{CO}}{P_{H_2}}.\frac{V_{H_2}}{V_{CO}},$$

where V_{H_2} is the rate of evaporation of hydrogen from a completely covered surface. In the cases considered, where we are dealing with the evaporation of a gas from a solid surface, the rate of evaporation from a completely covered surface may be regarded as a simple function of the vapour pressure. It follows that for various surfaces the rates of evaporation of gases are not the same, and we must postulate, as Langmuir has done, quasi-chemical combination between gas and surface, these quasi-chemical combinations possessing different free energies. Since little is known about the unstable hydrides of the elements, the work of Sieverts (*Zeitsch. physikal. Chem.*, 1907, **60**, 169, *et seq.*; see

lso D. P. Smith, *J. Physical Chem.*, 1918, **23**, 186) being devoted
o the study of occlusion of this gas in the various metals, we may,
or purposes of comparison, regard the free energies of the unstable
quasi-chemical superficial hydrides or carbonyls as equal or running
parallel to their heats of formation and stability, whilst a know-
edge of the vapour pressures at different temperatures and the
specific heats is required for an exact determination of the free
energy at various temperatures.

It will be noted that the ratio H_2/CO burnt increases pro-
gressively with the following catalytic materials: iron oxide; iron
oxide with promoters; copper oxide; nickel; palladium; this is
the order of increase in the stability of the hydrides, the union of
palladium and hydrogen being actually exothermic at the ordinary
temperature. The rate of evaporation of hydrogen from these
surfaces, V_{H_2}, will therefore, under identical conditions, decrease
in the above order, or the surface concentration, a_{H_2}, will increase.
Hence the ratio a_{CO}/a_{H_2}, which is the ratio of the surface concen-
trations of the two gases, will alter with the catalytic material,
and with this alteration in the surface concentrations there will
be a corresponding alteration in the rates of combustion. As the
temperature is raised, the rates of evaporation of the gases increase,
and thus the specific influence of the catalytic material disappears;
this inference is clearly indicated in the curves, where it will be
noted that at 400° the ratio is practically independent of the
catalyst employed.

Summary.

The selective combustion of carbon monoxide in hydrogen on
the surface of catalytic materials is shown to be a case of two
simultaneous reactions. The rates of combustion of the two gases
between 100° and 400° are related to the composition of the gaseous
mixture by the expression:

$$\frac{-\dfrac{dc_{CO}}{dt}}{-\dfrac{dc_{H_2}}{dt}} = K\frac{(CO)}{(H_2)(O_2)^{\frac{1}{2}}}.$$

Elevation in temperature causes a decrease in the apparent
selective character of the reaction, and the relationship between
the influence of temperature and the ratio of gases burnt can be
calculated approximately from the conception of the critical incre-
ment as developed by Lewis.

The results obtained are in agreement with Langmuir's theory
of adsorption, in which the adsorbed layer is considered to be only

one molecule thick; but the surface concentration of each gas is found to be dependent, not only on the nature of the gas, but also of the absorbing surface, indicating that the quasi-chemical combinations between gas and surface possess different free energies and are not simply the result of differences in activation of the reacting gaseous constituents.

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LXXXV.—*The Temperature of Explosion for Endothermic Substances.*

By RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE.

BERTHELOT has shown (*Compt. rend.*, 1887, **105**, 1159; 1899, **129**, 926) that certain endothermic substances which, if heated gradually, would either volatilise or decompose, can be made to explode by throwing them into a vessel previously raised to a suitably high temperature. This result was observed with trinitrophenol, mono-, di-, and tri-nitronaphthalene, and potassium chlorate. The authors, following up these observations of Berthelot, find that for each endothermic substance there is a temperature below which explosive decomposition does not occur, and this definite point is termed the temperature of explosion.

The procedure adopted was to drop a small quantity of the substance to the bottom of a clean test-tube immersed in a bath of potassium hydrogen sulphate just when the temperature of the bath has attained the temperature particular to each substance, as otherwise a simple decomposition would take place. The temperature of this bath, up to 500°, was recorded on a mercury thermometer; at higher temperatures, a thermo-couple was employed. The experiment was carried out in an atmosphere of carbon dioxide, but any other indifferent gas, such as nitrogen, may be used, and explosive decomposition occurs with equal readiness in a vacuum.

From the results recorded below for the temperatures of explosion of various substances, one or two conclusions of a general kind may be drawn. So far as nitro-derivatives are concerned, it appears that, of the disubstituted derivatives of benzene, the ortho compound, as a rule, has the lowest, and the para-compound the highest, temperature of explosion. Thus the temperatures of explosion for *o*-, *m*-, and *p*-chloronitrobenzene are 614°, 638°, and

720° respectively. In the case, however, of the nitrophenols, the para-compound has a lower temperature of explosion than the meta-compound. For dinitro-compounds with the nitro-group in the meta-position, the temperature of explosion falls as the number of alkyl groups attached to the ring increases. In this connexion, the figures for the temperatures of explosion of m-dinitrobenzene, 2:4-dinitrotoluene, and 4:6-dinitro-o-xylene may be quoted: they are 580°, 470°, and 438° respectively. The same relation holds good in the case of trinitro-derivatives.

In the following record, the temperature of explosion follows the name of the compound examined.

Nitro-compounds.

o-Dinitrobenzene, 472°; m-dinitrobenzene, 580°; 1:3:5-trinitro-benzene, 520°; 2:4-dinitrotoluene, 470°; a-2:4:6-trinitrotoluene, 118°; 4:6-dinitro-o-xylene, 438°; 3:4-dinitro-o-xylene, 413°; trinitroxylene (m. p. 178°), 408°; 2:4:6-trinitro-m-xylene, 410—412°; 2:3:6-trinitro-p-xylene, 410°; dinitromesitylene, 418°; trinitromesitylene, 415°; trinitrocumene, 502°; 2:4-dinitrostilbene, 412°; o-dinitrostilbene, 420°; a-dinitrodiphenylmethane (m. p. 181°), 335°; 1:6-dinitronaphthalene, 492°; 1:8-dinitronaphthalene, 445°; trinitronaphthalene (m. p. 122°), 364°; tetranitronaphthalene (m. p. 170°), 323°; o-chloronitrobenzene, 614°; m-chloronitrobenzene, 638°; p-chloronitrobenzene, 720°; p-bromonitrobenzene, 755°; p-iodonitrobenzene, 605°; o-nitroaniline, 655°; m-nitroaniline, 552°; p-nitroaniline, 627°; 2:4-dinitroaniline, 548°; p-nitrobenzoic acid, 635°; 2:4-dinitrobenzoic acid, 484°; 3:5-dinitrobenzoic acid, 523°; o-nitrophenol, 630°; m-nitrophenol, 657°; p-nitrophenol, 633°; 2:4-dinitrophenol, 498°; 2:4:6-trinitrophenol, 418°; 3-nitro-o-cresol, 503°; 6-nitro-m-cresol, 393°; 3:4-dinitro-o-cresol, 472°; 3:5-dinitro-o-cresol, 455°; 2:4:6-trinitro-m-cresol, 405°; 5-nitro-p-xylenol, 407°; 3:5-dinitro-o-xylenol, 432°; 2:4:6-trinitroresorcinol, 314°; o-dinitrodihydroxydiphenyl (m. p. 184°), 47°; 2:6-dichloro-4-nitrophenol, 548°; 4:6-dichloro-2-nitrophenol, 62°; 2:6-dibromo-4-nitrophenol, 625°; 4:6-dibromo-2-nitrophenol, 30°; 2:4:6-tribromo-3-nitrophenol, 605°; 6-bromo-2:4-dinitrophenol, 713°; 2-iodo-3-nitrophenol, 448°; 2:4-di-iodo-6-nitrophenol, 533°; 2:6-di-iodo-4-nitrophenol, 548°.

Picrates.

Ammonium picrate, 423°; hydrazine picrate, 385°; allylamine picrate, 270°; carbamide picrate, 489°; semicarbazide picrate,

474°; guanidine picrate, 498°; hexamethylenetetramine picrate, 360°; aniline picrate, 398°; *o*-toluidine picrate, 400°; α-naphthol picrate, 458°; β-naphthol picrate, 469°; naphthalene picrate, 484°; phenanthrene picrate, 478°; acenaphthene picrate, 418°; pyridine picrate, 432°; quinine picrate, 280°; quinidine picrate, 272°; cinchonine picrate, 268°; cinchonidine picrate, 260°; strychnine picrate, 290°; atropine picrate, 460°.

Azo-compounds.

Azobenzene, 540°; aminoazobenzene, 598°; dimethylaminoazobenzene, 643°; diazoaminobenzene, 703°.

Haloid Compounds.

Iodoform, 295°; *p*-di-iodobenzene, 788°; 2:4:6-tri-iodophenol, 675°; di-iodo-*o*-cresol, 782°; 2:4:6-tri-iodo-*m*-cresol, 696°; 2:4:6-tribromoresorcinol, 713°; 2:4:6-tribromo-orcinol, 793°; pentabromo-orcinol, 698°.

Organic Perchlorates.

Allylamine perchlorate, 262°; methylamine perchlorate, 338°; propylamine perchlorate, 290°; heptylamine perchlorate, 265°; hexylamine perchlorate, 278°; aniline perchlorate, 250°.

o-Toluidine perchlorate.—This salt has not previously been described. It is prepared by neutralising the base with perchloric acid. It does not melt on heating, but slowly carbonises:

0·0993 gave 6 c.c. N_2 at 28° and 760 mm. N = 6·72.

$C_7H_9N,HClO_4$ requires N = 6·76 per cent.

It explodes at 260°.

m-Toluidine perchlorate.—This salt was prepared by the interaction of the hydrochloride of the base and silver perchlorate. It melts and chars at 200°:

0·0804 gave 4·9 c.c. N_2 at 28° and 760 mm. N = 6·78.

$C_7H_9N,HClO_4$ requires N = 6·76 per cent.

It explodes at 300°.

The following perchlorates were prepared by double decomposition, as in the preceding case.

p-Toluidine perchlorate:

0·1027 gave 6·2 c.c. N_2 at 29° and 760 mm. N = 6·70.

$C_7H_9N,HClO_4$ requires N = 6·76 per cent.

It explodes at 278°.

m-4-*Xylidine perchlorate* decomposes at 200°:

0·1000 gave 5·8 c.c. N_2 at 28° and 760 mm. $N = 6·45$.

$C_8H_{11}N,HClO_4$ requires $N = 6·33$ per cent.

It explodes at 260°.

p-*Xylidine perchlorate* decomposes at 210°:

0·1072 gave 6 c.c. N_2 at 28° and 760 mm. $N = 6·33$.

$C_8H_{11}N,HClO_4$ requires $N = 6·33$ per cent.

It explodes at 258°.

Benzylamine perchlorate melts at 120°:

0·0816 gave 5·2 c.c. N_2 at 28° and 760 mm. $N = 7·09$.

$C_7H_9N,HClO_4$ requires $N = 6·76$ per cent.

It explodes at 305°.

Phenylethylamine perchlorate, 280°; α-naphthylamine perchlorate, 228°; menthylamine perchlorate, 308°.

Camphylamine perchlorate melts and decomposes at 215°:

0·0570 gave 3·1 c.c. N_2 at 29° and 760 mm. $N = 5·97$.

$C_{10}H_{19}N,HClO_4$ requires $N = 5·53$ per cent.

It explodes at 255°.

Diethylamine perchlorate melts at 107° and is very hygroscopic:

0·1067 gave 7·8 c.c. N_2 at 28° and 760 mm. $N = 8·13$.

$C_4H_{11}N,HClO_4$ requires $N = 8·09$ per cent.

It explodes at 282°.

Dipropylamine perchlorate, 308°; diamylamine perchlorate, 323°; benzylethylamine perchlorate, 322°; benzylmethylamine perchlorate, 294°.

Dibenzylamine perchlorate explodes at 290°:

0·0574 gave 2·6 c.c. N_2 at 27° and 760 mm. $N = 5·31$.

$C_{14}H_{15}N,HClO_4$ requires $N = 4·7$ per cent.

p-*Tolyltrimethylammonium perchlorate* melts at 192°:

0·0670 gave 3·8 c.c. N_2 at 30° and 760 mm. $N = 6·08$.

$C_{10}H_{16}N,ClO_4$ requires $N = 5·62$ per cent.

It explodes at 310°.

Methylpyridinium perchlorate explodes at 362°:

0·0661 gave 4·9 c.c. N_2 at 32° and 760 mm. $N = 8·12$.

C_6H_9N,ClO_4 requires $N = 7·61$ per cent.

Ethylpyridinium perchlorate explodes at 340°:

0·0765 gave 4·9 c.c. N_2 at 30° and 760 mm. $N = 7·07$.

$C_7H_{11}N,ClO_4$ requires $N = 6·73$ per cent.

Neurine perchlorate, 298°; phenylbenzylmethylammonium perchlorate, 275°; trimethylsulphonium perchlorate, 280°; ethylquinolinium perchlorate, 330°; propylquinolinium perchlorate,

342°; ethylquinaldinium perchlorate, 268°; hydrazine monoperchlorate, 238°; hydrazine diperchlorate, 215°; trimethylenediamine perchlorate, 310°; ethylenediamine perchlorate, 270°.

Guanidine perchlorate melts at 237°:

0·2249 gave 53 c.c. N_2 at 29° and 760 mm. N = 26·15.

$CH_5N_3,HClO_4$ requires N = 26·41 per cent.

It explodes at 367°.

Semicarbazide perchlorate explodes at 278°:

0·0929 gave 20·2 c.c. N_2 at 30° and 760 mm. N = 24·01.

$CH_5ON_3,HClO_4$ requires N = 24·00 per cent.

Piperazine perchlorate melts at 80°:

0·1156 gave 9 c.c. N_2 at 29° and 760 mm. N = 8·64.

$C_4H_{10}N_2,2HClO_4,2H_2O$ requires N = 8·69 per cent.

It explodes at 290°.

o-*Phenylenediamine perchlorate* explodes at 250°:

0·0310 gave 2·6 c.c. N_2 at 27° and 760 mm. N = 9·31.

$C_6H_8N_2,2HClO_4$ requires N = 9·09 per cent.

m-Phenylenediamine perchlorate, 263°; p-phenylenediamine perchlorate, 260°.

Alkaloids, etc.

Brucine, 793°; narcotine, 720°; narceine, 697°; chloralurethane, 673°; oxalylhydrazide, 548°; acetophenoneoxime, 734°; benzil, 643°.

Investigations on similar lines are being continued.

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LXXXVI.—*The Preparation of Butylamine and of n-Dibutylamine. The Separation of Aliphatic Amines by Partial Neutralisation.*

By EMIL ALPHONSE WERNER.

THE preparation of n-butylamine, and of n-dibutylamine, from the interaction of butyl bromide and ammonia in alcoholic solution at the ordinary temperature has been investigated. A procedure similar to that employed in the preparation of the corresponding ethyl derivatives of ammonia was adopted (T., 1918, **113**, 899).

The details of a few experiments on a simple method for the
separation of amines from intermediate distillates are recorded, and
whilst the results have a practical value as regards the economic
preparation of amines on a large scale, they go to show that the
prevailing views with respect to the relative basicity of primary,
secondary, and tertiary aliphatic amines require to be modified.
(Expts. 2, 3, and 4.)

EXPERIMENTAL.

n-Butyl bromide was conveniently prepared by distillation at
98—100° of a mixture of butyl alcohol, sulphuric acid, and sodium
bromide in molecular proportions, the temperature being raised to
120° towards the end of the process. The yield of the crude product,
dried over calcium chloride, was equal to 92 per cent. of the theo-
retical, and from 1126 grams there were obtained after redistillation
1082 grams of pure butyl bromide, boiling at 100—101°.

Expt. I.—Four litres of 90 per cent. alcohol were saturated with
ammonia until 500 grams of the gas had been dissolved; 200 grams
of butyl bromide were added (ratio butyl bromide to NH_3 approxi-
mately 1 to 20), after which, at successive intervals of three days,
fresh quantities of the alkyl haloid were added as follows: 180, 170,
160, 150, and finally 140 grams. Thus, in all, 1000 grams were
added over a period of fifteen days; preliminary tests had shown
that nearly all of the butyl bromide was decomposed after three
days. Only a few crystals of ammonium bromide separated, and on
the twentieth day the alcoholic solution was concentrated by dis-
tillation, when 175 grams of ammonium bromide were recovered.
As no crystalline matter separated after further concentration, the
product was diluted with water and boiled to expel the last traces of
alcohol. A dark brown, syrupy liquid (1200 grams) was ultimately
obtained, which, analysis showed, contained 399·4 grams of bromine;
hence this required 200 grams of sodium hydroxide for the libera-
tion of the total amines present.

Whilst the separation of butylamine (b. p. 76°) from dibutylamine
(161°) by distillation was comparatively simple, this was not so as
regards the separation of the latter from tributylamine (214°).
Hence, in order to avoid tedious fractionations of a mixture of all
three amines, fractional treatment with sodium hydroxide was
adopted as a preliminary (T., *loc. cit.*).

The product was introduced into a large separating funnel,
40 grams of sodium hydroxide dissolved in 80 c.c. of water were
added, and the mixture was vigorously agitated at intervals; after a
few hours the layer of 'amine' which had separated was removed.

It weighed 67 grams (dry) and was a mixture of di- and tri-butyl-amine, in which the latter largely predominated; it was dealt with as described later. (Amine A, Expt. 2.)

After the addition of 80 grams of sodium hydroxide to the residual liquid, followed by brisk agitation, 200 grams of 'amine' (B) were separated. This was distilled, with the aid of a three-bulb pear-shaped still-head, and 109 grams of pure dibutylamine were collected, after 49 grams had passed over between 80° and 158° (dealt with under Expt. 3). The residue, 42 grams, boiling above 161° was added to 'amine' (A). To the remaining solution a final quantity of 80 grams of sodium hydroxide was added, the mixture was transferred to a flask, and the whole of the liberated amine was removed by distillation at 90°. The product, 'amine' (C), weighed 187 grams (dry); it was redistilled, using a three-column evaporator still-head, and 167 grams of pure butylamine (76—77°) were collected. The residue (20 grams) was added to the first distillate (49 grams) from 'amine' (B).

Separation of a Mixture of Dibutylamine and Tributylamine, by Partial Neutralisation with Hydrochloric Acid.

The separation of the mixture of 'amine' (A) with the residue from 'amine' (B) into its constituents by fractional distillation was abandoned as hopeless; thus, for example, whilst the greater part passed over before the boiling point (214°) of tributylamine was reached, the first fraction (162—180°) contained 10·7 per cent. of tributylamine, and the last fraction (200—214°) contained 16·6 per cent. of dibutylamine.

The following simple procedure gave the desired result:

Expt. 2.—The mixture, 98 grams, which on analysis was found to contain 51 grams of dibutylamine, was placed in a separating funnel and 132 c.c. of 3N-hydrochloric acid * and 40 c.c. of water were added. The product was thoroughly agitated, and after a few hours the layer of insoluble amine was removed. It weighed 46 grams, and distilled steadily at 212—214°; it was therefore pure tributyl-amine.

The aqueous solution was evaporated at 100°, and the residue dried over sulphuric acid; it weighed 64·3 grams and contained Cl = 21·46, whilst $(C_4H_9)_2NH,HCl$ requires Cl = 21·45 per cent.

The separation of the two amines was therefore complete.

* The amount of hydrochloric acid required to combine with the dibutyl-amine only; the extra water was necessary to keep the salt in solution.

Separation of a Mixture of Butylamine and Dibutylamine by Partial Neutralisation with Hydrochloric Acid.

Expt. 3.—The fraction collected between 80° and 158° (49 grams) from the distillation of 'amine' (B) and the residue (20 grams) from the distillation of 'amine' (C) were mixed. Analysis showed that the product contained approximately 48 grams of butylamine. It was well agitated with 220 c.c. of 3N-hydrochloric acid in a separating funnel and allowed to remain for twenty-four hours. The solution was extracted twice with 70 c.c. of ether to remove all the free amine. The ethereal solution (previously dried) was distilled, and after removal of the solvent and of a few c.c. of amine which passed over below 161°, 18 grams of pure dibutylamine were collected.

The aqueous solution was evaporated at 100°, and the residue dried over sulphuric acid. It contained $Cl = 31.14$, whilst $C_4H_9 \cdot NH_2, HCl$ requires $Cl = 32.42$ per cent. The weight was 74 grams, and the proportion of butylamine hydrochloride was equal to 86.2 per cent. Whilst the separation in this case was not so complete as in Expt. 2, the results show that on a manufacturing scale the recovery of amines from intermediate distillates and residues could be economically effected by this method.

The total yields of the respective amines were: butylamine, 215 grams = 40.2 per cent.; dibutylamine, 181 grams = 41.1 per cent.; and tributylamine, 47 grams = 10.4 per cent. of the theoretical. When 200 grams of butyl bromide were added to 3 litres of 90 per cent. alcohol, saturated with ammonia as in Expt. 1, and the product worked up after five days, 73 grams of butylamine, equal to 68.5 per cent. of the theoretical, were obtained; the yield of dibutylamine was 28 grams, equal to 31.9 per cent. of the theoretical, and no tributylamine was formed.

The following *n*-butyl derivatives were incidentally prepared in connexion with other work:

Ethyl *n*-butylcarbamate, $C_4H_9 \cdot NH \cdot CO_2Et$, from the interaction of butylamine and ethyl chloroformate dissolved in benzene, was obtained in theoretical yield as a colourless oil which boiled at 202—203°/765.5 mm. (van Erp, *Rec. trav. chim.*, 1895, **14**, 1, gives 200°/15 mm.).

Dibutylcarbamyl chloride, $(C_4H_9)_2N \cdot COCl$, a colourless oil, which boiled at 242—243°/755 mm., and became pink on exposure to air, was obtained from the interaction of carbonyl chloride and dibutylamine dissolved in benzene.

Tributylcarbamide, $C_4H_9 \cdot NH \cdot CO \cdot N(C_4H_9)_2$, was obtained as a viscous, colourless liquid which boiled at 238—239°/766 mm., by the

P P*

action of butylamine on the foregoing compound dissolved in benzene.

as-*Dibutylcarbamide*, $NH_2 \cdot CO \cdot N(C_4H_9)_2$.—The preparation of this derivative furnished an interesting example of the use of benzene in obtaining an anhydrous solid as described by Atkins and Wilson (T., 1915, **107**, 916); and the details are perhaps worth recording. Potassium cyanate was added to an aqueous solution of dibutylamine hydrochloride, and a viscous oil separated rapidly when the solution was heated to 100°. The oil, which was readily soluble in alcohol, ether, chloroform, or benzene, showed no signs of crystallisation * after it had remained for three days in a desiccator over sulphuric acid. The addition of light petroleum to the cold solution in benzene failed to induce crystallisation, and with the object of removing the solvent the mixture was distilled from a flask plunged in hot water. When a portion of the solvent had passed over as a turbid mixture, a sudden copious separation of needle-shaped crystals, melting at 149—150°, took place, while the liquid was still warm.

Found: $N = 16 \cdot 11$. $C_9H_{20}ON_2$ requires $N = 16 \cdot 28$ per cent.

The compound is very hygroscopic; it liquefies after exposure to the air for a few minutes.

Separation of Diethylamine from Triethylamine by Partial Neutralisation with Hydrochloric Acid.

The following experiment supplies a further illustration of the use of this method.

Expt. 4.—In the preparation of a considerable quantity of diethylamine, a fraction was collected between 75° and 91°; it had the composition $NHEt_2 = 6 \cdot 74$ per cent., $NEt_3 = 93 \cdot 26$ per cent. It weighed 146 grams, and therefore contained $9 \cdot 84$ grams of diethylamine. It was mixed with 67 c.c. of 2N-hydrochloric acid and treated as described in Expt. 3.

The free amine was collected without loss and boiled at 90—91°, the boiling point of pure triethylamine.

The hydrochloride recovered from the aqueous solution contained $Cl = 32 \cdot 22$, whilst $(C_2H_5)_2NH,HCl$ requires $Cl = 32 \cdot 42$ per cent.

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DUBLIN.   [*Received, July 23rd*, 1919.]

* Monobutylcarbamide melts at 86°; disubstituted carbamides of the above type generally melt at a much higher temperature than the monosubstituted derivatives.

LXXXVII.—*The Abnormal Behaviour of Glyoxaline-carboxylic Esters and Anilides towards Diazonium Salts.*
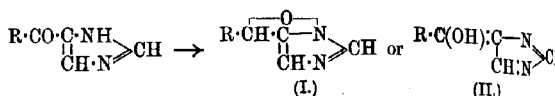
By ROBERT GEORGE FARGHER and FRANK LEE PYMAN.

In a recent paper (this vol., p. 217), we put forward evidence showing that glyoxalines are only capable of coupling with diazonium salts when they contain a free imino-group and also a hydrogen atom or some other displaceable group, such as the carboxyl group, in one of the 2-, 4-, or 5-positions. Numerous derivatives of glyoxaline, in which these conditions are fulfilled, have been shown to couple with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate, but an exceptional behaviour is shown by the esters of 5-methylglyoxaline-4-carboxylic acid (Gerngross, *Ber.*, 1912, **45**, 513) and the esters of glyoxaline-4-carboxylic acid (Pyman, T., 1916, **109**, 186). These give a negative result, whereas the corresponding acids behave normally, giving deep red solutions with the reagent.

With the object of finding some clue to this abnormality, we have examined the behaviour of a number of carboxylic acids containing the glyoxaline nucleus and their esters towards sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate. All the acids examined gave a positive result, and so also did the esters of those acids, such as glyoxalineacetic acid, in which the carbonyl group is separated from the glyoxaline nucleus by a chain of one or more carbon atoms. The esters of the 2-alkylglyoxaline-4-carboxylic acids, however, like those of glyoxaline-4-carboxylic acid and 5-methylglyoxaline-4-carboxylic acid, gave a negative result, and so also did the anilides of glyoxaline-4-carboxylic acid and its 2-alkyl derivatives. In order to ensure that the difference in behaviour was not due to the particular conditions selected for the test, the action of benzene-diazonium chloride and *p*-nitrobenzenediazonium chloride on glyoxaline-4-carboxylic acid and ethyl glyoxaline-4-carboxylate was examined. In the presence of hydrochloric acid or acetic acid, either of the derivatives coupled, whilst in the presence of sodium carbonate or sodium hydroxide the acid coupled but the ester did not.

The abnormality is thus seen to be connected with the direct attachment of the carboxyalkyl or carboxyanilide group to the glyoxaline nucleus, and would seem to be due to the mutual influence of the imino- and carbonyl groups.

Further than this we do not as yet feel able to offer any explan ation of the abnormality. The fact that all the glyoxalinecarb oxylic esters and anilides behave normally towards silver nitrate in ammoniacal solution, yielding insoluble silver salts, rules out a formula such as (I) not containing a free iminic or acidic hydrogen atom, whilst their stability towards potassium permanganate acid solution would appear to indicate that they exist as true glyoxalines in the presence of mineral acids.

$$R \cdot CO \cdot C \cdot NH \atop CH \cdot N \!\!>\!\! CH \ \rightarrow \ R \cdot CH \cdot \overset{\overline{\ O\ }}{\underset{CH \cdot N}{\overset{|}{C}} \!\!\!-\!\!N} \!\!>\!\! CH \ \text{or} \ R \cdot C(OH) : C \!\!-\!\! N \atop CH : N \!\!>\!\! C$$

$$\qquad\qquad\qquad\qquad\qquad (I.) \qquad\qquad\qquad (II.)$$

There is, however, the possibility of a molecular rearrangement such as that represented by formula (II), taking place under the influence of alkalis. The nitroglyoxalines also fail to couple with diazonium salts, and here the explanation seems clear, since these compounds dissolve in alkalis with a yellow colour, yielding salts which are no doubt derived from the corresponding nitronic acid as Windaus (*Ber.*, 1909, **44**, 758) has suggested, and no longer contain an imino-group.

$$NO_2 \cdot C \cdot NH \atop CH \cdot N \!\!>\!\! CH \ \underset{\text{acid}}{\overset{\text{alkalis}}{\rightleftarrows}} \ NaO_2N : C \!\!-\!\! N \atop CH : N \!\!>\!\! CH.$$

The glyoxalinecarboxylic esters and anilides, however, yield colourless solutions with alkalis, and although, bearing in mind that the nitroglyoxalines themselves are colourless and their alkaline solutions only comparatively pale yellow, the lack of colour would alone seem insufficient to preclude a formula such as (II), we do not feel justified in advancing it as more than a possibility until further experimental evidence has been accumulated.

While seeking for comparable instances of the mutual influence of imino- and carbonyl groups, we have observed that whereas anthranilic acid couples with sodium diazobenzene-*p*-sulphonate or *p*-nitrobenzenediazonium chloride in sodium carbonate solution ethyl anthranilate gives a negative result. Both, of course, couple in acid solution. Further, it is perhaps worth noting that whereas the hydrochloride of anthranilic acid is stable in aqueous solution the hydrochlorides of its methyl and ethyl esters are readily hydro lysed in cold aqueous solution with liberation of the free ester (com pare Kolbe, *J. pr. Chem.*, 1884, [ii], **30**, 474; Fränkel and Spiro *Ber.*, 1895, **28**, 1686; E. and H. Erdmann, *Ber.*, 1899, **32**, 1213) and whilst s-ethylenebisanthranilic acid dissolves readily in dilute

mineral acids, the corresponding methyl ester is insoluble even in excess (Fränkel and Spiro, *loc. cit.*).

EXPERIMENTAL.

The esters described in this communication were prepared by boiling the acids with absolute alcohol saturated with hydrogen chloride. After removing the excess of alcohol and adding cold saturated aqueous potassium carbonate, the esters of the 2-alkyl-glyoxaline-4-carboxylic acids separated in a crystalline state. The other esters were extracted from the solutions by means of chloroform, and crystallised either as base or as hydrogen oxalate.

Ethyl 2-methylglyoxaline-4-carboxylate crystallises from ethyl acetate in clusters of fine, shimmering needles, which melt at 156° (corr.) and are anhydrous. It is sparingly soluble in water, but readily so in alcohol or ethyl acetate.

Found: $C = 54\cdot3$; $H = 6\cdot7$; $N = 17\cdot9$.

$C_7H_{10}O_2N_2$ (154·1) requires $C = 54\cdot5$; $H = 6\cdot5$; $N = 18\cdot2$ per cent.

The ester gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

2-Ethylglyoxaline-4-carboxylic Acid and its Derivatives.

2-Ethylglyoxaline-4-carboxyanilide is prepared from 2-ethyl-glyoxaline-4:5-dicarboxylic acid in a yield amounting to 45 per cent. of the theoretical by the general method described in a previous communication (this vol., p. 217). It is readily soluble in alcohol but very sparingly so even in boiling water, from which it crystallises in clusters of fine needles; these are anhydrous and melt at 193° (corr.), sintering from 190°. It gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found: $C = 66\cdot6$; $H = 5\cdot8$; $N = 19\cdot2$.

$C_{12}H_{13}ON_3$ (215·2) requires $C = 66\cdot9$; $H = 5\cdot6$; $N = 19\cdot5$ per cent.

2-Ethylglyoxaline-4-carboxylic acid is obtained in good yield by the hydrolysis of the corresponding anilide by dilute hydrochloric acid at 130°. It is readily soluble in hot water, but sparingly so in cold, and crystallises from the former in well-defined, prismatic needles which contain two molecules of water of crystallisation. After drying at 110°, it melts at 252° (corr.), sintering from 248°. It gives an immediate blood-red coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found, in air-dried acid: loss at $110° = 20\cdot7$

$C_6H_8O_2N_2,2H_2O$ requires 20·5 per cent.

In acid dried at 110°, $C = 51.3$; $H = 5.7$; $N = 19.9$.

$C_6H_8O_2N_2$ (140·1) requires $C = 51.4$; $H = 5.8$; $N = 20.0$ per cent.

The *picrate* crystallises from water in large, prismatic needles containing one and a-half molecules of water of crystallisation. After drying at 60° in a vacuum, it sinters above 170° and forms a turbid liquid, which becomes clear at about 195°.

Found, in air-dried salt, $H_2O = 6.9$.

$C_6H_8O_2N_2, C_6H_3O_7N_3, 1\frac{1}{2}H_2O$ requires 6·8 per cent.

In dried salt, $N = 18.7$.

$C_6H_8O_2N_2, C_6H_3O_7N_3$ (369·2) requires $N = 19.0$ per cent.

Ethyl 2-ethylglyoxaline-4-carboxylate crystallises from ethyl acetate, in which it is readily soluble, in prismatic needles which melt at 129° (corr.), and are anhydrous. It is readily soluble in alcohol, but sparingly so in water. It gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found: $C = 56.8$; $H = 7.2$; $N = 16.5$.

$C_8H_{12}O_2N_2$ (168·2) requires $C = 57.1$; $H = 7.2$; $N = 16.6$ per cent.

2-Phenylglyoxaline-4-carboxylic Acid and its Derivatives.

2-Phenylglyoxaline-4-carboxyanilide is prepared by the action of boiling aniline on 2-phenylglyoxaline-4 : 5-dicarboxylic acid in a yield amounting to 74 per cent. of the theoretical. As it is practically insoluble in boiling water, it is left behind after the steam distillation somewhat contaminated by resinous impurities, which are readily removed by grinding and washing with ice-cold alcohol. It is sparingly soluble in alcohol or the other usual organic solvents, and separates from alcohol in minute, glistening needles, which melt at 263° (corr.) and are anhydrous. It gives no coloration with sodium diazobenzene-*p*-sulphonate in sodium carbonate solution.

Found: $C = 72.6$; $H = 5.3$; $N = 15.9$.

$C_{16}H_{13}ON_3$ (263·2) requires $C = 73.0$; $H = 5.0$; $N = 16.0$ per cent.

2-Phenylglyoxaline-4-carboxylic acid is obtained in good yield by the hydrolysis of the corresponding anilide, which, however, is much more stable towards acid hydrolysis than the 2-alkyl derivatives. At 130° the reaction proceeds very slowly, but at 145—150° the reaction is complete after eight to nine hours' heating. The acid separates from boiling water, in which it is fairly readily soluble, in fan-shaped clusters of minute needles containing one and a-half molecules of water of crystallisation. After drying at 110°, it melts and effervesces at 239° (corr.). The acid gives an immediate

red coloration with sodium diazobenzene-p-sulphonate in sodium carbonate solution.

Found, in air-dried material: loss at $110° = 12.7$.

$1\frac{1}{2}H_2O$ requires 12·6 per cent.

In substance dried at 110°, $C = 63.5$; $H = 4.5$; $N = 14.8$.

$C_{10}H_8O_2N_2$ (188·1) requires $C = 63.8$; $H = 4.3$; $N = 14.9$ per cent.

Ethyl 2-phenylglyoxaline-4-carboxylate crystallises from ethyl acetate in minute needles, which melt at 189° (corr.), sintering above 183°. It is readily soluble in alcohol or hot ethyl acetate, less readily so in cold ethyl acetate, and very sparingly so in water. It gives no coloration with sodium diazobenzene-p-sulphonate in sodium carbonate solution.

Found, in air-dried substance: loss at $100° = 9.5$.

Found, in dried substance: $C = 66.5$; $H = 5.7$; $N = 12.9$.

$C_{12}H_{12}O_2N_2$ (216·1) requires $C = 66.6$; $H = 5.6$; $N = 13.0$ per cent.

Ethyl Glyoxaline-4-acetate.—This was prepared previously by the action of alcoholic hydrogen chloride on 4-cyanomethyl-glyoxaline (T., 1911, **99**, 681), and can also be obtained by the esterification of the corresponding acid or by the action of alcohol on the hydrochloride of glyoxaline-4-acetyl chloride. It gives a deep red colour when mixed with sodium diazobenzene-p-sulphonate in aqueous sodium carbonate.

Glyoxaline-4-acetyl chloride hydrochloride can be prepared in a crystalline state by the method given below. The crude product contains less than the theoretical amount of chlorine, and we have been unable to devise a satisfactory method of purifying it.

Five grams of phosphorous pentachloride and 6 c.c. of thionyl chloride were heated on the water-bath to incipient ebullition (about 50°), and 4 grams of glyoxaline-4-acetic acid hydrochloride were added, the mixture being well stirred. Evolution of hydrogen chloride took place, and the pasty mass quickly became crystalline, forming minute leaflets. When the reaction had ended, the mass was diluted with chloroform, filtered, washed with chloroform, and dried in a vacuum over sulphuric acid and sodium hydroxide. The dry, crystalline powder obtained in this way was pale pink and amounted to 4·4 grams, that is, 97·7 per cent. of the theoretical. The specimen with the highest chlorine content melted and decomposed at 127° (corr.), the others at 125°.

Found: $C = 33.2$; $H = 3.5$; $Cl = 35.5$, 35·1, 36·8 (in different specimens).

$C_5H_5ON_2Cl,HCl$ (181·0) requires $C = 33.2$; $H = 3.3$; $Cl = 39.2$ per cent.

Ethyl β-Glyoxaline-4-propionate.—This was purified by crystallisation of the hydrogen oxalate from alcohol. The ester formed an oil, which gave an immediate blood-red colour with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

The *hydrogen oxalate* separates from alcohol in colourless, shimmering leaflets, which are anhydrous and melt at 160° (corr.) after sintering from 155°. It is readily soluble in water or hot alcohol, but sparingly so in cold alcohol.

Found : $C = 48.1$; $H = 6.0$; $N = 11.8$.

$(C_8H_{12}O_2N_2)_4(C_3H_2O_4)_3$ (942·7) requires $C = 48.4$; $H = 5.8$; $N = 11.9$ per cent.

Ethyl a-hydroxy-β-glyoxaline-4-propionate crystallises from dry chloroform in minute, colourless plates which melt at 118—119° (corr.), and are anhydrous. It is readily soluble in water or alcohol, sparingly so in chloroform, and insoluble in ether. It gives a cherry-red colour with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

Found : $C = 52.3$; $H = 6.5$.

$C_8H_{12}O_3N_2$ (184·1) requires $C = 52.2$; $H = 6.6$ per cent.

LXXXVIII.—*The Free Energy of Dilution of Aqueous Sodium Chloride Solutions.*

By ARTHUR JOHN ALLMAND and WILFRID GUSTAV POLACK.

THIS work, which was commenced a few months prior to the outbreak of war, was undertaken with the view of investigating systematically the relations existing between activity and concentration for the different molecular species present in aqueous solutions of typical binary electrolytes, working between the limits of saturated solutions and solutions of dilution only determined by difficulties of measurement. G. N. Lewis, to whom we owe the introduction into thermodynamics of the term "activity" (*Zeitsch. physikal. Chem.*, 1907, **61**, 129), has also provided a very convenient way of expressing the deviations—true or apparent—from the laws of perfect solutions which are exhibited by the ions and by the molecules of undissociated electrolyte, namely, by the use of the magnitude "activity coefficient." The "activity coefficient" of a

chemical species in any phase is the ratio activity/concentration for that species in the given phase. In the case of electrolytes, activity can be measured by any of the related thermodynamic methods (that is, osmotic pressure, lowering of freezing point, electromotive force), whilst the concentration can be determined from conductivity methods, with or without the rather uncertain correction for viscosity. The extent to which the activity coefficient differs from unity and changes in magnitude with change of concentration is a measure of the abnormality of the thermodynamic behaviour of the chemical species in question under the experimental conditions.

The same author (*J. Amer. Chem. Soc.*, 1912, **34**, 1631), in an important critical survey of the subject, discusses the then available experimental data, including measurements of solubility product, depression of freezing point, and electromotive force. Assuming the validity of the conductivity method of arriving at concentration values, the conclusion drawn is that, whilst in very dilute solutions concentrations and activities of ions are directly proportional, their activity coefficients fall off somewhat as the solutions become more concentrated. On the other hand, the activity coefficients of the undissociated molecules of electrolytes increase rapidly with increase of concentration. Specific effects for ions would appear to enter at concentrations higher than $0.1N$. Later in his paper, he seriously disputes the basis of the Kohlrausch method of arriving at the ionic and undissociated-molecule concentrations, believing it to be vitiated by changes in the mobility of ions with concentration, a view first put forward by Jahn (*Zeitsch. physikal. Chem.*, 1900, **33**, 545). His final conclusion is that ionic activities and concentrations are proportional in dilute solutions up to $0.1N$, the activity coefficients therefore being unity, throughout this region.

These views have been much discussed during the last few years. The conclusion generally drawn (see, for example, Bates, *J. Amer. Chem. Soc.*, 1915, **37**, 1421) is that the conductance–viscosity ratio is a measure of concentration, leaving unexplained the undoubted discrepancies between activity and concentration even in dilute solutions. When the present measurements were undertaken, however, the matter had still to be regarded as an open one. One point which it was hoped to elucidate was the magnitude of the specific effects, if any, in the variations of the activity coefficients of the ions with concentration. By making measurements with four different electrolytes, such as MA, MB, NA, and NB, and by comparing these with one another at concentrations at which the ionic concentrations in the solutions of the four different electro-

lytes, as determined by the conductance–viscosity ratio, are identical, it should be possible to test this point for the ions M', N', A', and B'. Hitherto, the assumption—a probable one—has been made that the activities of the two ions are identical in any solution of a binary electrolyte where their concentrations, excluding complex-formation and solvation, are necessarily the same.

The electromotive force method of measurement was chosen. Tolman and Ferguson * ($J. Amer. Chem. Soc.$, 1912, **34**, 232) had already used it successfully for measurements of activity coefficient on dilute aqueous solutions of hydrochloric acid. It was intended to use as electrolytes the chlorides, bromides, iodides, hydroxides, and sulphates of sodium, potassium, and lithium, and one of the authors had already found (T., 1914, **105**, 1941) the amalgam electrodes prepared according to the directions of G. N. Lewis and his co-workers ($J. Amer. Chem. Soc.$, 1910, **32**, 1459; 1912, **34**, 119) to function satisfactorily.

The principle of the method is briefly as follows. If two cells are set up,

| (1) Electrode reversible to ion A. | Solution of AB. Concentration C_1. | Electrode reversible to ion B. |
| (2) Electrode reversible to ion A. | Solution of AB. Concentration C_2. | Electrode reversible to ion B. |

the electrode systems being identical, and the two combinations only differing in the values of the concentrations C_1 and C_2 ($C_1 > C_2$), the difference between the electromotive forces of the two cells (E) is a measure of the free energy of dilution of AB from the concentration C_1 to the concentration C_2. If the ions are both univalent, the free energy of dilution per gram-molecule is expressed by

$$FE = RT \ln \frac{[a_1]_{\text{undiss.}}}{[a_2]_{\text{undiss.}}} = RT \ln \frac{[a_1]_A \cdot [a_1]_B}{[a_2]_A \cdot [a_2]_B},$$

where a represents activity and the suffixes refer to the two solutions and to the undissociated molecules and the different ions. Making the assumption mentioned above that $[a]_A = [a]_B$ for the same solution, we have

$$FE = 2RT \ln \frac{[a_1]_{\text{ion}}}{[a_2]_{\text{ion}}}.$$

The measurements of electromotive force allow, therefore, the immediate calculation of activity ratios for the solutions concerned, and from these, using concentration data obtained from measure-

* **Professor G. N. Lewis informed us by letter that Professor Tolman had no intention of continuing the work further.**

ments of conductivity, the activity coefficient ratios follow immediately.

In order to calculate heats of dilution, measurements were carried out at 18° and 25°. Their close proximity was compensated for by the possibility of utilising the existing conductivity data for calculations of concentration.

Measurements with sodium chloride were completed before the end of 1914. It has been impossible to resume the work, and the results are consequently published as they stand.

Several papers dealing with the same or with closely related problems have been published in America in the interval. Such are those of Bates (*loc. cit.*), MacInnes and Parker (*J. Amer. Chem. Soc.*, 1915, **37**, 1445), Forbes and Anderegg (*ibid.*, 1676), Harned (*ibid.*, 2460; 1916, **38**, 1986; 1918, **40**, 1461), Ellis (*ibid.*, 1916, **38**, 787), Ferguson (*J. Physical Chem.*, 1916, **20**, 326), Linhart (*J. Amer. Chem. Soc.*, 1917, **39**, 615, 2601), Noyes and Ellis (*ibid.*, 2532), Pearce and Mortimer (*ibid.*, 1918, **40**, 509), and Rodebush (*ibid.*, 1204). Some of these will be referred to later.

EXPERIMENTAL.

The sodium amalgam was prepared precisely as described by Lewis and Kraus (*loc. cit.*), except that the mercury was distilled over more rapidly on to the sodium by enclosing the containing vessel in an asbestos oven, the mercury being heated to about 280° and the sodium to 130°. The mercury employed, both for making the amalgams, as also for the calomel electrodes, was purified by passing at least twice down the usual column of acid mercurous nitrate. The amalgam was indistinguishable from mercury in appearance, and remained so for more than four years.

The amalgam electrode vessels were as designed by Lewis and Kraus. The calomel electrode vessels used were chiefly (see, however, later) of the usual Ostwald type, the connecting tubes being made as short and as wide as practicable in order to diminish the resistance. The calomel, after being washed several times by shaking with a small quantity of the solution and a little mercury, was shaken with a larger quantity of the solution, the liquid with the calomel in suspension being drawn into the carefully cleaned and dried electrode vessels. From four to six electrodes were prepared for each concentration of sodium chloride solution for which the electromotive force was measured, and, after allowing time for their potentials to become constant (usually eighteen hours), they were compared against one another. Electrodes which agreed at 18° were always found to agree at 25°. When several electrodes

had been obtained showing a maximum difference between any pair of about 0·3 millivolt, one of them was chosen for the actual measurements (or one for the measurements at 18° and another for 25°), and generally compared again with the others after the measurements.

In all, seven concentrations of sodium chloride were employed, namely, 5·41N (saturated at 18°),* 3N, N, 0·5N, 0·1N, 0·02N, and 0·01N. The solutions were made up to volume at 18°. With solutions of concentration 0·5N and above, the measurements can readily be carried out with considerable accuracy. The solution is contained in a glass tube 10 cm. long and 3·5 cm. in diameter, suitably clamped in the thermostat, and into this tube dip the nozzles of the amalgam and calomel electrodes, also clamped to separate stands. The essential parts of the calomel electrode are also in the thermostat. While the measurement is being made, amalgam drops very slowly from the nozzle of the electrode, and the electromotive force remains practically constant.

With the more dilute solutions, however, several difficulties arise. The most serious of them is the decomposition of the amalgam on coming into contact with the solution. As pointed out by Lewis and Kraus, the decomposition takes place chiefly on small specks floating on the surface of the amalgam, and when the electrode has been in use for a minute or so, these are carried away. Nevertheless, the amalgam which collects at the foot of the tube containing the solution continues to decompose, and there is always some visible decomposition at the nozzle of the electrode, even when the surface seems to be perfectly clean. This tends to make the potential of the electrode less negative in two ways, namely, (i) by increasing the sodion concentration in the liquid surrounding the nozzle of the electrode, and (ii) by decreasing the sodium concentration in the surface layers of the amalgam. The effect of (i) obviously increases rapidly with increasing dilution, not only because of the increase in the actual rate of decomposition, but also because of the relatively larger effect produced on the concentration of the sodions. The consequence of (ii) is that the potential fluctuates, rising suddenly as each drop of amalgam becomes detached, exposing a fresh surface. To counteract this, it is necessary to allow the amalgam to flow more rapidly from the electrode, and this means still more decomposition in the liquid. In consequence of these facts, it was found necessary for the measurements with dilute solutions to use an apparatus of the type shown in Fig. 1, in which the product of decomposition is

* This solution was actually made up to saturation, and its concentration calculated from the available data, not experimentally determined.

prevented from accumulating round the electrode. In its first form, solution flowed from a large dropping funnel into the tube T, and up through the siphon tube S. The amalgam dropping from the electrode N collected at A, the alkali formed by the decomposition being thus carried away from the electrode, which was always surrounded by fresh solution. Hydrogen produced at A collected at B. C is the calomel electrode described below.

FIG. 1.
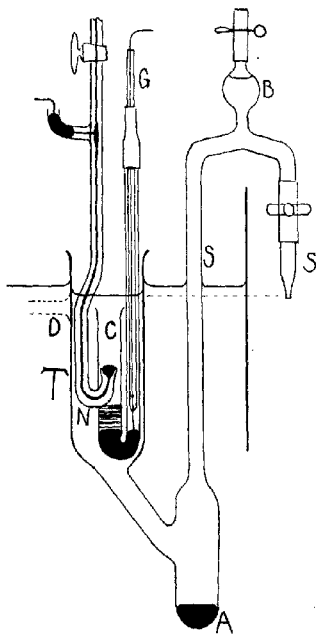
Later, the apparatus was modified so that the solution did not flow directly into the tube T, but passed first through a close-wound spiral of thin-walled tubing immersed in the thermostat and sealed into the tube T at D. With the $0·01N$-solution, the flow of electrolyte at the moment of measurement must be fairly rapid, and this precaution becomes essential to ensure that the temperature of the solution is accurately that of the thermostat.

Another difficulty which arises with the more dilute solutions is

the comparatively high resistance of the ordinary type of calomel electrode. For the 0·01N-measurements, the form shown in Fig. 1 was employed. C is the electrode vessel proper, contact being made with the mercury by means of a platinum wire sealed into the end of a narrow glass tube, G. When the electrode was not actually in use, the mouth of the tube C was closed by a cork, a little of the liquid being removed by a pipette, care being taken not to disturb the calomel at the foot of the tube. These electrodes had a much lower resistance than the others, but were less trustworthy. Several were made up for preliminary tests, and in one or two instances considerable variations occurred, probably due to mechanical disturbances. With suitable precautions, however, they proved satisfactory enough.

In the present investigation, it appeared that the limit of dilution was reached at 0·01N, owing to the decomposition of the amalgam. Much greater disturbances occurred between individual readings than in any of the other cases. The electromotive force tended to increase with increasing rate of flow of the electrolyte,* even until the latter reached the maximum possible with the apparatus used, so that the effect of decomposition was apparently never quite eliminated. The figures given for this dilution are therefore less trustworthy than any of the others. One would expect these to be, if anything, too low. The values obtained by extrapolation would also appear to indicate this. They are probably more trustworthy than the experimental values, and are used instead of these in subsequent calculations.

The electromotive forces were measured with a Clark-Fisher potentiometer and cadmium cell, both of which had been tested at the National Physical Laboratory. The potentiometer could be read to 0·0001 volt as long as the resistance in the circuit was not excessively high. Potentiometer, galvanometer, cells, etc., and also the stands to which the electrodes were clamped, were all carefully insulated on glass.

In all, three different amalgams were prepared, each being contained in a pair of electrodes. In each measurement several readings were taken with each electrode with various rates of flow of the amalgam, and, where the special apparatus was used (0·1N and more dilute solutions), with various rates of flow of electrolyte. The difference between the values obtained for the two electrodes was in every case less than the possible experimental errors due to other sources. The figures given represent in each

* Incidentally this shows that the flowing electrolyte had reached the temperature of the bath, as the electromotive force increases with rise of temperature.

case the mean of the various individual readings with the two electrodes (in some cases of two or more complete sets of such readings), together with the maximum error likely to be involved, taking into account the variations in the individual readings in the calomel electrodes themselves, etc.

The three pairs of electrodes contained amalgams with the following respective percentages of sodium:

$$(a)\ 0{\cdot}2234\,;\ (b)\ 0{\cdot}1657\,;\ (c)\ 0{\cdot}1389.$$

These values were determined by weighing out small quantities of the amalgam, acidifying, and, on completion of the decomposition, estimating the excess of acid by titration.

The electrodes (a) contained only a small quantity of amalgam, and were only used for two dilutions, namely, $0{\cdot}1N$ and $0{\cdot}02N$. As the measurements were carried out with stationary electrolyte and not with the special apparatus, there was a fair amount of decomposition. The values must therefore be regarded as more or less preliminary. Nevertheless, there is good agreement between the values for the difference of electromotive force at $0{\cdot}1N$ and $0{\cdot}02N$ furnished by the two pairs of electrodes (a) and (b), the special apparatus being used in the case of (b).

Tables I and II give the actually measured electromotive forces in volts at 18° and 25° for the three amalgams (a), (b), and (c).

TABLE I.

18°.

Concentration.	(a)	(b)	(c)
5·41N	—	—	2·0281±0·0002
3N	—	—	2·0770±0·0001
1N	—	2·1466±0·0002	2·1398±0·0002
0·5N	—	2·1792±0·0003	—
0·1N	2·2635±0·0010	2·2534±0·0004	—
0·02N	2·3384±0·0010	2·3274±0·0005	—
0·01N	—	—	2·350 ±0·002

TABLE II.

25°.

Concentration.	(a)	(b)	(c)
5·41N	—	—	2·0283±0·0001
3N	—	—	2·0784±0·0001
1N	—	2·1499±0·0002	2·1430±0·0002
0·5N	—	2·1838±0·0003	—
0·1N	2·2710±0·0010	2·2596±0·0003	—
0·02N	2·3450±0·0010	2·3336±0·0010	—
0·01N	—	—	2·358 ±0·002

Assuming that the difference in potential between amalgams (b) and (c) as deduced from the readings with N-solutions is $0{\cdot}0068$

volt at 18° and 0·0069 volt at 25°, the values which the electro-motive forces would have for amalgam (c) and 0·5N-, 0·1N-, and 0·02N-solutions can be calculated. They are contained in table III and are plotted in Fig. 2. In view of what has already been said (see p. 1026), the figures for 0·01N-solutions given in the table are not the experimental values, but those extrapolated from the curve.
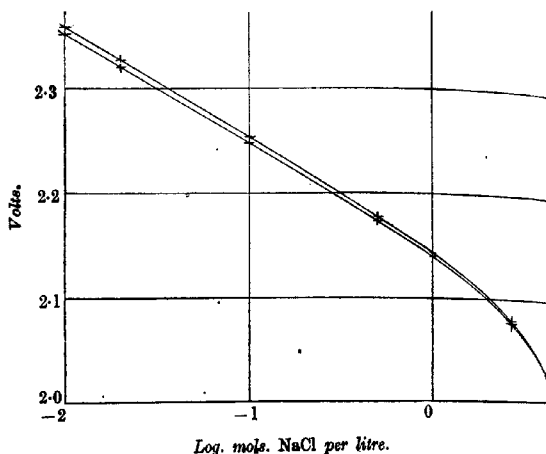
FIG. 2.

Log. mols. NaCl *per litre.*

TABLE III.

E.M.F. for the combination
Hg | Hg₂Cl₂ aqueous
NaCl | 0·1389 per cent.
sodium amalgam.

C in mols. NaCl per litre.	C in mols. NaCl per 1000 grams of water.	18°. Volts.	25°. Volts.	a (defined by $e_t = e_{18}[1 + (t - 18)a]$
5·41	6·12	2·0281	2·0283	141 × 10⁻?
3·0	3·196	2·0770	2·0784	963
1·0	1·022	2·1398	2·1430	2140
0·5	0·5034	2·1724	2·1769	2960
0·1	0·1003	2·2466	2·2527	3880
0·02	0·02003	2·3206	2·3267	3760
0·01	0·01001	2·3520	2·3585	3950
		(±0·0005)	(±0·0005)	

Free and Total Energy Changes of Cell Reaction.

Taking the Faraday as 96,540 coulombs, the decreases in free and total energy of the system per gram-equivalent transformed can be calculated for the cell reaction

$2Na$ (in form of $0·1389$ per cent. amalgam) $+ Hg_2Cl_2 \longrightarrow$
$2Hg + 2NaCl$ (in aqueous solution)
from the figures in table III. The results are contained in table IV.

TABLE IV.

C in mols. NaCl per 1000 grams of water.	Free energy decrease at		Total energy decrease at 18°. Joules.
	18°. Joules.	25°. Joules.	
6·12	195795	195815	195000
3·196	200520	200650	195030
1·022	206575	206885	193690
0·5034	209725	210160	191600
0·1003	216885	217475	192360
0·02003	224030	224620	199500
0·01001	227060	227695	200790

The figures indicate that the decrease of total energy, or heat effect of the reaction, at first falls off as the electrolyte becomes more dilute, and then commences to increase. The results are plotted in Fig. 3, and it will be seen that the curve has a minimum at about $0·25—0·3$ molecule of sodium chloride per 1000 grams of water. Too much stress, however, is not laid on this result, or on certain other calculations of heat effects recorded subsequently in this paper. The range of temperature over which measurements were made is small, and the calculations are correspondingly affected, whilst for the more dilute solutions the possible errors in the measurements must be seriously taken into account.

Sodium Chloride Concentration Cells without Transference.

By subtracting the values of electromotive force given in table III from the corresponding values for the $0·1N$-solution, figures are obtained for the electromotive forces of sodium chloride concentration cells "without transference," one of the two solutions in every case being $0·1N$ (p. 1022). These values are contained in table V.

TABLE V.

C in mols. NaCl per 1000 grams of water.		$E.M.F.$ at		α (defined by e_t. $= e_{18}[1+(t-18)\alpha]$).
C_1.	C_0.	18°. Volts.	25°. Volts.	
6·12	0·1003	0·2185	0·2244	386×10^{-5}
3·196	,,	0·1696	0·1743	396
1·022	,,	0·1068	0·1097	388
0·5034	,,	0·0742	0·0758	308
0·02003	,,	−0·0740	−0·0740	0
0·01001	,,	−0·1054	−0·1058	54

We can compare these figures with those obtained by other in-vestigators for similar cells.   Thus, whilst for $\frac{C_1}{C_0} = \frac{0\cdot1}{0\cdot01}$ (normal concentrations) sodium chloride gives a figure of $0\cdot1058$ volt at $25°$, other experimenters have obtained the following figures for hydrochloric acid and for potassium and lithium chlorides:
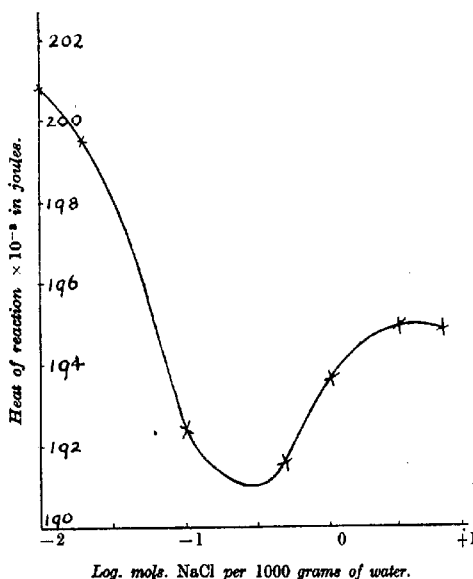
Fig. 3.

Log. mols. NaCl *per* 1000 *grams of water.*

TABLE VI.

Electrolyte.	Volt.	Observer.
HCl	0·114	Noyes and Ellis (*loc. cit.*)
KCl	0·1089	MacInnes and Parker (*loc. cit.*)
LiCl	0·10433	Pearce and Mortimer (*loc. cit.*)

By a comparison of the figures for such cells with those given by the corresponding cells with transference, the transport number of the electrolyte can be calculated.   The electromotive force of the cell without transference (p. 1022) is $e_1 = 2\frac{RT}{F} ln \frac{a_1}{a_2}$, whilst that of the cell with transference is $e_2 = 2N\frac{RT}{F} ln \frac{a_1}{a_2}$, where N is the

cation transport number if electrodes reversible to the anion are employed. Consequently,

$$N_c = \frac{e_2}{e_1}$$

Measurements of sodium chloride concentration cells with transference were carried out at 18° by Jahn (*Zeitsch. physikal. Chem.*, 1902, **41**, 298), using calomel electrodes and dilute solutions of electrolyte. Table VII contains figures taken from his paper, together with corresponding values drawn from table V or Fig. 2. In the last column are the calculated transport numbers for the sodium ion.

TABLE VII.

C_1 in mols. per litre.	C_2 in mols. per litre.	e_1.	e_2.	N_c.
0·02	0·01	0·0314	0·01293	0·412
0·04	0·02	0·0317	0·01268	0·400
0·06	0·03	0·0318	0·01255	0·394

Experimental determinations gave the following results (Abegg, "Handbuch," II, i, 231):

C.	$t°$.	N_c.	Observer.
3—5N.	10°	0·352	Hittorf.
0·7N.	16	0·366	,,
0·005N.	10	0·379	,,
1/30—1/150N.	0	0·387	Jahn-Schulz.
1/8—1/14N.	18	0·395	,,
1/8—1/150N.	30	0·404	,,

In a way exactly similar to that by which the figures in table V were obtained from the data of table III, we can calculate from table IV values for the decrease in total energy (heat content) and free energy associated with the transfer of one molecule of sodium chloride from any concentration given in the table to a 0·1 molar normal solution. Table VIII contains the results.

TABLE VIII.

C in mols. NaCl per 1000 grams of water.		Free energy decrease in joules at		Total energy decrease in joules at
C_1.	C_0.	18°.	25°.	18°.
6·12	0·1003	21090	21660	−2640
3·196	,,	16365	16825	−2870
1·022	,,	10310	10590	−1330
0·5034	,,	7160	7315	+760
0·02003	,,	−7145	−7145	−7145
0·01001	,,	−10175	−10220	−8430

In table IX, the results in the last column of table VIII are expressed as the total energy decrease attending the transfer of

one molecule of sodium chloride from a concentration of $6\cdot12$ molecules per 1000 grams of water to other concentrations given in the first column.

TABLE IX.

C in mols. NaCl per 1000 grams of water.	Heat effect at 18°.	
	Joules.	Calories.
6·12	—	—
3·196	+30	+7
1·022	−1310	−313
0·5034	−3400	−812
0·1003	−2640	−630
0·02003	+4505	+1075
0·01001	+5790	+1382

The curve representing the variation of the heat effects of tables VIII and IX with concentration of electrolyte will, of course, be exactly similar in form to that in Fig. 3. The magnitude of the possible errors involved must again be emphasised. This point is also brought out by the last column in table V. It is improbable that the value of a, after approximating to the "ideal" figure of $366\cdot5 \times 10^{-5}$ in concentrated solutions, should fall and fluctuate in the dilute solutions, as the experimental figures appear to indicate.

The free energies of dilution of sodium chloride at 25° from saturated solution to $1\cdot0N$ and from $1\cdot0N$ to $0\cdot1N$ have been calculated by Rodebush (*loc. cit.*) from freezing-point measurements to be respectively 2477 and 2464 calories.

Our value for $-\Delta F_{298}$ from $1\cdot0N$ to $0\cdot1N$ can be obtained from column four of table VIII, and is $10590/4\cdot189 = 2528$ cals., a rather higher figure. A saturated solution of sodium chloride at 25° is $5\cdot43N$, and contains $6\cdot14$ molecules per 1000 grams of water (as against $5\cdot41N$ and $6\cdot12$ molecules per 1000 grams at 18°). If we extrapolate to this concentration on Fig. 2, we obtain the value $2\cdot0279$ for the electromotive force in volts of the experimental cell at 25°. From this figure and that for the cell with saturated solution at 18°, we calculate for the reaction

$$2Na \text{ (in form of } 0\cdot1389 \text{ per cent. amalgam)} + Hg_2Cl_2 \longrightarrow 2Hg + 2NaCl \text{ (solid)}$$
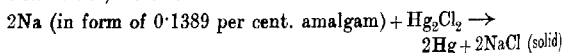
that $-\Delta F_{298}$ is 195,775 joules and $-\Delta H_{291}$ is 196,585 joules, in both cases for the transformation of 1 gram-equivalent. From this value of $-\Delta F_{298}$ and from $-\Delta F_{298}$ for a $1\cdot0N$-solution (table IV, column three), we calculate that $-\Delta F_{298}$ from saturated solution to $1\cdot0N$ is $11,110/4\cdot189 = 2652$ calories, a much higher figure than that of Rodebush.

The difference of the above value of $-\Delta H_{291}$ for the reaction

involving the production of solid sodium chloride and that of $-\Delta H_{291}$ for the reaction involving the production of saturated sodium chloride solution (see table IV) furnishes us with the heat of solution of one molecule of sodium chloride in a saturated solution at 18°. This value comes to 195,000—196,585 joules, or −378 calories. There are no experimental determinations with which this figure can be directly compared. Using the van't Hoff isochore, and taking the solubility of sodium chloride as 35·79 grams and 35·92 grams per 100 grams of water at 18° and 25° respectively, we calculate the heat of solution as −89·5 calories, a far smaller value. The assumption of the validity of the gas laws, however, involved in this equation is certainly not justified, and we believe our value to be nearer the truth.

If we compare the values deduced from our curve for heats of solution in given quantities of water and for heats of dilution with experimental values, the concordance is only moderate. For the heat of solution of one molecule of sodium chloride in 9·2 molecules of water, Stackelberg (Landolt-Börnstein, "Tabellen," 4th edition, p. 875) found −410 calories; for the same in 10 molecules of water, van Deventer and van de Staat (*Zeitsch. physikal. Chem.*, 1892, **9**, 55) found −475 calories. We deduce, respectively, −371 and −373 calories. For the heat of solution of one gram-molecule of sodium chloride in 100 gram-molecules of water, Thomsen (Landolt-Börnstein, "Tabellen," 4th edition, p. 875), Stackelberg (*Zeitsch. physikal. Chem.*, 1898, **26**, 545), and van Deventer and van de Staat found, respectively, −1180 calories, −1030 calories, and −1130 calories. Our value is −1110 calories. When, however, we compare the different values for heats of dilution over concentration limits included in this range, the discrepancies are large. We get much smaller heat effects for dilution up to concentrations of one molecule of sodium chloride to 20 molecules of water, and much larger for dilutions between $1NaCl:50H_2O$ and $1NaCl:100H_2O$. Thus van Deventer and van de Staat found the molar heat of dilution from $1NaCl:10H_2O$ to $1NaCl:20H_2O$ to be −247 calories, whereas our figure is −17 calories. Similarly, their value for dilution from $1NaCl:50H_2O$ to $1NaCl:100H_2O$ is −128 calories per mol. NaCl. Our value is −463 calories.

The Reaction $2Na + Hg_2Cl_2 \longrightarrow 2NaCl + 2Hg$.
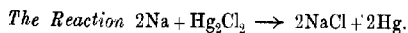
Lewis and Kraus (*loc. cit.*) found that 0·2062 per cent. amalgam at 25° is 0·8456 volt positive to metallic sodium, whilst the temperature-coefficient of the electromotive force of the combina-

tion is -0.0000408 volt/degree. It follows that the amalgam is 0.8459 volt positive to sodium at $18°$.

The measurements in tables I and II show that our amalgam (c) is 0.0068 volt positive to (b) at $18°$, and that (b) is 0.0110 volt positive to (a). At $25°$, the potential differences are 0.0069 and 0.0114 volt respectively. Plotting these figures and interpolating to find the relative potentials of the 0.2062 per cent. amalgam at these two temperatures, we obtain the result that it is negative to the amalgam (c) (0.1389 per cent.) by 0.01465 volt at $18°$ and 0.01495 volt at $25°$. Combining these values with the figures of Lewis and Kraus, it follows that amalgam (c) is positive to sodium by 0.86055 volt at both $18°$ and $25°$. From the electromotive forces of the cells, amalgam (c) | saturated $NaCl$ | Hg_2Cl_2 | Hg, experimentally determined for $18°$ and extrapolated for $25°$, we calculate for the cell

$$Na \,|\, \text{saturated } NaCl \,|\, Hg_2Cl_2 \,|\, Hg$$
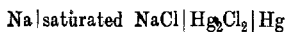
that

$$e_{291} = 2.88865 \text{ volts,}.$$
$$e_{298} = 2.88845 \quad \text{,,}$$

and for the cell reaction

$$2Na + Hg_2Cl_2 \longrightarrow 2NaCl \text{ (solid)} + 2Hg$$
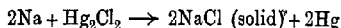
that

$$-\Delta F_{291} = 66,573 \text{ calories}$$
$$-\Delta F_{298} = 66,569 \quad \text{,,}$$
$$-\Delta H_{291} = 66,740 \quad \text{,,}$$

per gram-equivalent transformed. The "calorimetric" value of $-\Delta H_{291}$ is obtained by subtracting the accepted heat of formation of $\frac{1}{2}Hg_2Cl_2$ (Varet) from the heat of formation of $NaCl$ (Thomsen), that is, $31,315$ from $97,700$, leading to a figure of $66,385$ cals.

Free Energy in Solution of One Molecule of Sodium Chloride.

By adding to the above values of $-\Delta F$ for the reaction

$$2Na + Hg_2Cl_2 \longrightarrow 2NaCl + 2Hg$$
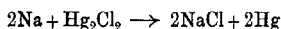
the values of $-\Delta F$ for the reaction

$$2Hg + Cl_2 \text{ (one atmosphere)} \longrightarrow Hg_2Cl_2,$$
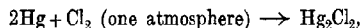
that is, $25,255$ and $25,125$ cals. per gram-equivalent at $18°$ and $25°$ respectively (Ellis, *loc. cit.*, p. 757), we arrive at once at values for the difference in free energy between sodium and chlorine on the one hand and solid sodium chloride on the other, namely, for the reaction
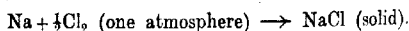
$$Na + \frac{1}{2}Cl_2 \text{ (one atmosphere)} \longrightarrow NaCl \text{ (solid)}.$$
$$-\Delta F_{291} = 91,828 \text{ calories}.$$
$$-\Delta F_{298} = 91,694 \quad \text{,,}$$

As a check on these values, we can calculate $-\Delta H_{291}$. The value found is 97,400 cals., whilst the calorimetric value already referred to above is 97,700 cals.

We are now in a position to state the values of the free energy of one molecule of sodium chloride at different dilutions in aqueous solution, taking the free energies of the two elements concerned, sodium and chlorine, as zero. The figures are contained in table X, and are obtained by combining the above values for the free energy of solid sodium chloride with the figures in table VIII and the value deduced on p. 1032 for $-\Delta F_{298}$ from saturated to $1 \cdot 0N$-sodium chloride. Similar figures for the total energy of a molecule of sodium chloride could also be calculated, but the data are not regarded as sufficiently trustworthy.

TABLE X.

C in mols. per litre	Free energy of 1 mol. of NaCl in calories at	
	18°.	25°.
(saturated).	−91828	−91694
3·0	−92956	−32858
1·0	−94401	−94346
0·5	−95154	−95128
0·1	−96863	−96874
0·02	−98568	−98580
0·01	−99292	−99314

Activities of Ions and Undissociated Molecules.

From the data contained in table V, activity ratios can be calculated by the method given on p. 1022. This has been done, and the results are contained in table XI.

TABLE XI.

C in mols. per 1000 grams of water.	Activity NaCl$_c$ / Activity NaCl$_{0\cdot1003}$		Activity Na$_c^+$ / Activity Na$_{0\cdot1003}^+$		Activity of Na$^+$ (assuming value in 0·1003 solution is 0·073 at 25°).	Thermodynamic degree of dissociation.
	18°.	25°.	18°.	25°.	[25°.	25°.
6·12	6096·0	6249·0	78·1	79·05	5·771	0·94
3·196	867·0	874·4	29·44	29·57	2·159	0·67
1·022	70·8	71·7	8·414	8·468	0·618	0·60
0·5034	19·29	19·15	4·392	4·376	0·319	0·63
[0·1003	1·0	1·0	1·0	1·0	0·073	0·73]
0·02003	0·0522	0·0560	0·229	0·237	0·0173	0·86
0·01001	0·0149	0·0162	0·122	0·127	0·0093	0·93

From the ratios in columns two to five, and assuming with Harned (*J. Amer. Chem. Soc.*, 1918, **40**, 1461) that the most

likely value for the ionic activity of such an electrolyte as sodium chloride in $0.1N$-solution is 0.073, the values in columns six and seven are calculated. The term "thermodynamic degree of dissociation" to denote the ratio of ionic activity to total concentration seems preferable to "activity coefficient," as used by Ellis (*loc. cit.*). The latter term should be retained for expressing the ratio activity/concentration for the same molecular species, according to the nomenclature introduced by Lewis.

This table shows that the thermodynamic degree of dissociation first falls off as the concentration of the dissolved sodium chloride increases from $0.01N$, passes through a minimum value at about $1N$, and then increases to the high figure of 0.94 at the saturation point. This behaviour is shared qualitatively by aqueous hydrogen chloride and potassium chloride solutions. The former show a marked minimum for the value of the thermodynamic degree of dissociation at about $0.5N$ (Ellis, *loc. cit.*), whilst for potassium chloride solutions the lowest value lies at about $2N$ (Harned, *J. Amer. Chem. Soc.*, 1916, **38**, 1986).

Lithium chloride solutions have not yet been investigated over a sufficient range to discover a minimum, supposing one to exist.

Our values for this function can be compared with those obtained by Harned (*J. Amer. Chem. Soc.*, 1918, **40**, 1461) from measurements of sodium chloride concentration cells with transference. His figures are given in table XII, and the agreement with ours is seen to be good.

TABLE XII.

C of NaCl in mols. per litre.	Activity. $T=25°$.	Thermodynamic degree of dissociation.
3.0	2.261	0.754
2.0	1.397	0.698
1.0	0.628	0.628
0.5	0.312	0.624
0.3	0.192	0.64
[0.1	0.073	0.73]

The value of 0.0093 for the activity of the sodium ion in $0.01N$-solution, obtained on the assumption that the activity in $0.1N$-solution is 0.073, is identical with that assumed by Linhart (*J. Amer. Chem. Soc.*, 1917, **39**, 2601) for the activity of the potassium and hydrogen ions in $0.01N$-solutions. His assumption leads to ionic activities for these ions in $0.1N$-solutions of 0.078 and 0.082 respectively, figures considerably higher than the corresponding one for the sodium ion. If, however, we calculate the activity of the lithium ion in $0.1N$-solution from the results of

Pearce and Mortimer (*loc. cit.*), assuming that the activity in 0·01*N*-solution is 0·0093, we arrive at a figure of 0·070, still lower than that for sodium ions. The fact that the relative degrees of hydration of the four ions in question arrange themselves in the inverse order of magnitude to that of the activities in 0·1*N*-solution may be of significance.

Owing to the present lack of suitable viscosity data to apply to the existing conductivity measurements, no attempt can be made to calculate accurately the activity coefficients of the ions and un-dissociated molecules. It is, however, certain that, starting from dilute solutions, a/c for the ions at first decreases, passes through a minimum, and then increases, whilst a/c for the undissociated molecules increases throughout, and reaches very high values in concentrated solutions. Sodium chloride in this respect acts in a similar way to other electrolytes.

The different points of view from which the anomalies of strong electrolytes can at present most fruitfully be discussed are dealt with in the excellent papers of Bates, Pearce and Mortimer, Harned and others, already referred to, and there is no need to add anything here, particularly as there are still many gaps in absolutely necessary data unfilled.

Molecular Condition of Sodium in Sodium Amalgams.

Our experiments furnish an interesting confirmation of the work of Ramsay (T., 1889, **55**, 533) and of Cady (*J. Physical Chem.*, 1898, **2**, 551), who found by vapour pressure and electro-metric experiments, respectively, that sodium, dissolved in mercury at concentrations varying from 0·03 to 0·66 per cent., behaved as if it were giving an abnormally large number of osmotically active particles, that is, as if simple atoms were dissociated into something simpler. From table II, it will be seen that the electro-motive forces between amalgams (*a*) and (*b*), if measured in a sodium chloride solution at 25°, would amount to 0·0114 volt, and between (*b*) and (*c*) to 0·0069 volt. Substituting these values and those for the concentrations of the amalgams in the equation

$$e = \frac{2 \cdot 303 \, RT}{F} \cdot \frac{1}{x} \cdot \log \frac{c_1}{c_2}$$

where x represents the association factor of the metal atoms dis-solved in the mercury, we find for the combination amalgam (*a*)–amalgam (*b*) that x is 0·68, and for the combination amalgam (*b*)–amalgam (*c*) that x is 0·65. These values for x correspond with apparent molecular weights of 15·6 and 15·0 respectively. Ramsay,

working at high temperatures, found that the apparent molecular weight decreased as the concentration of sodium increased. For concentrations closely corresponding with ours, values of about 18 were obtained. Cady, working at 19—20°, and measuring amalgam concentration cells, using pyridine solutions as electrolytes, obtained figures from 11·3 to 16·3, again decreasing with increasing concentration of amalgam.

At first sight, it would seem possible that sodium atoms dissolved in mercury are dissociated into sodium ions and free electrons (the latter surrounded by a condensed atmosphere of mercury molecules), and that the electrical conductivity of sodium amalgams is partly electrolytic in nature. Such a state of affairs would be analogous to that shown by Kraus (*J. Amer. Chem. Soc.*, 1908, 30, 1323) to exist in solutions of sodium in liquid ammonia. Skaupy (*Zeitsch. physikal. Chem.*, 1907, **58**, 560), indeed, has tried to prove that the supposed equilibrium

$$\text{metal} \rightleftharpoons \text{metal ion} + \text{electron}$$

in dilute amalgams obeys the Ostwald dilution law. The experiments of Lewis, Adams, and Lanman (*J. Amer. Chem. Soc.*, 1915, **37**, 2656) are, however, completely against this assumption. They showed that, when a current passes through a sodium amalgam solution, the sodium concentrates at the positive pole. Their suggested explanation is rendered less probable by subsequent very exact experiments by Hine (*ibid.*, 1917, **39**, 882) on the conductivity of dilute alkali metal amalgams, but it is at all events clear that the dissolved sodium is not associated with a surplus positive electric charge.

The true explanation of the apparent low molecular weights is in all probability the formation of compounds between the sodium and the mercury. The importance of taking this into account was first pointed out by Haber (*Zeitsch. physikal. Chem.*, 1902, 41, 399). Sodium and mercury can combine to form the well-defined compound $NaHg_6$. Abegg ("Handbuch," II, i, 679) has shown that it is a likely assumption that the concentration of free mercury in the amalgams is thereby lowered to a sufficient extent to explain Ramsay's (and also the electrometric) results. Cady (*loc. cit.*) has further demonstrated that the abnormalities in the electrometric results disappear if the heat of dilution of the amalgams is taken into account. Actually measuring this for sodium amalgam between certain concentrations, he obtained very exact agreement. Low apparent molecular weights are associated with abnormally high electromotive forces for concentration cells, with positive heats of dilution, and with the formation of exothermic compounds.

Those interested are referred to papers by Richards and Garrod-Thomas (*Zeitsch. physikal. Chem.*, 1910, **72**, 165), and by Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 501), where the situation is clearly set out.

The temperature-coefficients of our own cells were measured over too small a range to allow of the calculation from them of the heats of dilution of the sodium amalgams used.
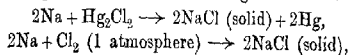
Summary.

(1) Measurements of cells of the type

$$Hg \,|\, Hg_2Cl_2 \text{ aqueous NaCl solutions} \,|\, \text{sodium amalgam}$$

have been carried out at 18° and 25° for concentrations of sodium chloride ranging between $0.01N$ and saturated solution.

(2) From these have been calculated the free and total energies of dilution of sodium chloride between the concentration limits referred to.

(3) The transport number of the sodium ion in different dilute sodium chloride solutions has been calculated.

(4) The molecular heat of solution of sodium chloride in saturated solution at 18° has been calculated.

(5) The changes in free and total energies of the reactions

$$2Na + Hg_2Cl_2 \longrightarrow 2NaCl \text{ (solid)} + 2Hg,$$

$$2Na + Cl_2 \text{ (1 atmosphere)} \longrightarrow 2NaCl \text{ (solid)},$$

have been calculated.

(6) The free energies of one molecule of sodium chloride in aqueous solution at various concentrations at 18° and 25°, referred to the free energies of the elements sodium and chlorine as zero, have been calculated.

(7) The "thermodynamic degrees of dissociation" of sodium chloride in aqueous solution at different concentrations at 25° have been calculated, together with the corresponding activities of the sodium ion.

(8) Confirmation has been obtained of previous work on the molecular condition of sodium in sodium amalgams.

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LXXXIX.—*The Active Substance in the Iodination of Phenols.*

By VICTOR COFMAN.

NUMEROUS methods are known for the preparation of iodophenols, and the entrance of iodine in the molecule has been accounted for in various ways. The object of this communication is to prove that hypoiodous acid is solely responsible for the iodination in a number of processes investigated, and to show that the presence of the above-mentioned substance as an intermediate compound satisfactorily explains the formation of iodophenols by the various known methods.

That hypoiodous acid has the property of reacting with phenols, producing iodo-substituted compounds, is no new discovery. Selivanov (*Ber.*, 1894, **27**, 1012) pointed out that the iodination of phenol by means of nitrogen iodide is due to the hydrolysis of the latter compound and the consequent production of hypoiodous acid; various other authors (Bray, *Zeitsch. physikal. Chem.*, 1906, **54**, 563; Cohn and Schultz, *Ber.*, 1905, **38**, 3294; Gardner and Hodgson, T., 1909, **96**, 1822) have suggested that the same compound may be responsible for the formation of iodophenols by the "iodine and alkali" methods, but no definite proofs have been adduced in support of this view, nor has it yet been attempted to ascribe the production of iodophenols in all the known instances to the presence of one and the same substance in the various reacting mixtures.

The earliest mention of any iodophenol is that made by Piria (*Compt. rend.*, 1843, **18**, 187), but the merit of a first investigation of this class of compounds rests with Lautemann (*Annalen*, 1861, **120**, 299), who prepared several iodophenols and iodo-salicylic acids. From his method of preparation, Lautemann inferred that, on heating iodine with salicylic acid, a direct substitution takes place, although he could not explain what happened to the displaced hydrogen.

Later, Kekulé (*Annalen*, 1864, **131**, 221) showed that the compounds obtained by Lautemann's process were formed only when the mixture of iodine and salicylic acid was dissolved in alkalis. He prepared the same compounds by the action of iodine and iodic acid on salicylic acid, and explained their formation thus:

(i) $C_7H_6O_3 + I_2 + KOH = C_7H_5O_3I + KI + H_2O.$

(ii) $5C_7H_6O_3 + 2I_2 + HIO_3 = 5C_7H_5O_3I + 3H_2O.$
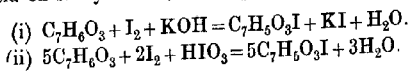
Kekulé's opinion was that iodine has the property of displacing the hydrogen atoms of certain organic compounds in the presence of a third substance capable of oxidising, or removing in some other fashion, the hydriodic acid formed during the reaction. This explanation has since been put forward to account for the formation of iodophenols by other methods, namely, (i) the "iodine and mercuric oxide" method (*Ber.*, 1872, **5**, 380); (ii) the "iodine and sodium phosphate" method (*J. Pharm. Chim.*, 1902, [vi], **15**, 217); (iii) the iodine monochloride method (*ibid.*).

According to this view, in every one of the above cases, the first part of the reaction is $HR + I_2 = IR + HI$ (where $R =$ phenolic radicle), and the second part consists in the removal of the hydriodic acid thus formed by the third substance present.

The production of iodo-substituted compounds by means of iodine monochloride was originally given a similarly simple interpretation (Brown, *Phil. Mag.*, 1854, [iv], **8**, 201):

$$HR + ICl = IR + HCl.$$
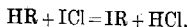
A more complicated equation was put forward by Dagener (*J. pr. Chem.*, 1879, [ii], **20**, 324) as representing the course of the reaction in his hypochlorite method of obtaining tri-iodoresorcinol:

$$6CaOCl_2 + 12KI + 12HCl + 2C_6H_4(OH)_2 =$$
$$6CaCl_2 + 6HI + 12KCl + 2C_6HI_3(OH)_2 + 6H_2O,$$
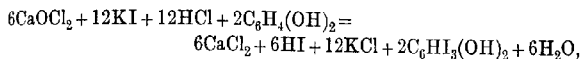
whilst in the "dry" reactions of Birnbaum (*Ber.*, 1882, **15**, 459) and Schall (*Ber.*, 1883, **16**, 1897), the authors assume that the hydrogen atom displaced by the iodine wanders in one case to the carboxyl, and in the other to the hydroxyl group, thus:

$$OH \cdot C_6H_4 \cdot CO_2H + I_2 = OH \cdot C_6H_3I \cdot CO_2H + AgI$$

and

$$C_6H_5 \cdot ONa + I_2 = C_6H_5 \cdot OI + NaI,$$
$$C_6H_5 \cdot OI \longrightarrow C_6H_4I \cdot OH.$$
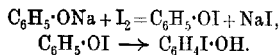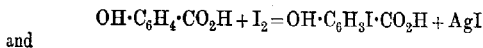
Finally, Willgerodt (*J. pr. Chem.*, 1888, [ii], **37**, 446) supplied for his method the equation

$$C_6H_5 \cdot OH + NI_3 = C_6H_2I_3 \cdot OH + NH_3.$$
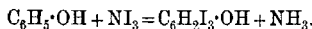
EXPERIMENTAL.

The opinion that the formation of iodophenols must be due to the presence of hypoiodous acid suggested itself to the present author during the preparation of di-iodosalicylic acid by the action of iodine monochloride on salicylic acid. It was observed, on the one hand, that the reaction did not take place in the absence of

water, whilst, on the other hand, an aqueous solution of iodine monochloride soon lost its power of combining with salicylic acid. The gradual disappearance of the "active iodine" (that is, iodine capable of attacking the phenolic molecule) from such a solution is strikingly shown in the table given below. The method employed was to add 10 c.c. of a solution of iodine monochloride in glacial acetic acid (Wijs' solution) to 100 c.c. of water; the mixture was allowed to remain at the ordinary temperature (12°) for the specified time, after which excess of sodium salicylate (5 c.c. of a 10 per cent. solution) was added to combine with the "active iodine"; this was followed after one minute by the addition of an excess of potassium iodide and titration with $N/10$-thiosulphate solution.

Table showing the Rapid Decrease in the Amount of "Active Iodine" Present in Aqueous Iodine Monochloride Solution.

Time solution was allowed to remain.	No. of c.c. of $N/10$-thiosulphate required.	"Active iodine."
0	0	27·8
10 sec.	4·1	23·7
20 ,,	5·8	22·0
30 ,,	7·3	20·5
1 min.	10·5	17·3
2 ,,	13·3	14·5
3 ,,	16·8	11·0
5 ,,	17·1	10·7
10 ,,	18·1	9·7
30 ,,	20·2	7·6
1 hr.	21·9	5·9
2 hrs.	23·3	4·5
16 ,,	25·1	2·7
24 ,,	26·2	1·6

How is this rapid decrease in the activity of iodine monochloride solutions explained? As is well known, iodine monochloride is partly hydrolysed in aqueous solution,

$$ICl + H_2O \rightleftarrows IOH + HCl,$$
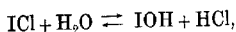
the hypoiodous acid formed quickly decomposing into iodic acid and free iodine, the reaction being usually represented thus:

$$5IOH = 2I_2 + HIO_3 + 2H_2O.$$
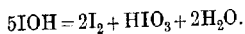
Now, it is highly probable that the decrease in the activity of the solution is due to this decomposition of the hypoiodous acid, but owing to our imperfect knowledge of the constitution of iodine monochloride solutions, this cannot be definitely proved. Other products of decomposition, such as the compound ICl,HCl and

iodine trichloride, are present, and these may have a bearing on the matter.

Nevertheless, it is quite clear that the present view, which ascribes the iodination of phenols in iodine monochloride solution to the action of the iodic acid formed, is untenable, since the amount of iodophenol produced actually diminishes as the concentration of iodic acid and free iodine increases.

The next step was to investigate the formation of iodophenols in alkaline iodine solutions. In this case, thanks to the fact that the kinetics· of the system iodine – potassium iodide – sodium hydroxide has been fully investigated by Schwickler (*Zeitsch. physikal. Chem.*, 1895, **16**, 303), Forster (*J. Physical Chem.*, 1903, **56**, 324), Bray (*Zeitsch. physikal. Chem.*, 1906, **54**, 563), and Skrabal (*Monatsh.*, 1907, **28**, 217; 1909, **32**, 167, 815), it is possible to show that, in such solutions, *the mass of "active iodine" is at any instant equal to the amount of hypoiodous acid present*, thus proving them conclusively to be one and the same substance.

Without going too deeply into the kinetics of hypoiodite solutions, it may be stated that the first reaction which takes place when iodine is dissolved in alkalis, namely,

$$I_2 + OH' \rightleftharpoons IOH + I',$$
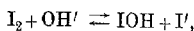
attains rapidly a state of equilibrium and, in strongly alkaline solutions, the concentration of free iodine is negligible. The decomposition of the resulting hypoiodous acid, on the contrary, is relatively slow, proceeding with measurable velocity. It has thus been found possible to prove that the reaction is one of the second order, the rate of change being expressed by the empirical formula

$$-\frac{d[IOH]}{dt} = \frac{[I'] + e(E)}{[OH']} \cdot ka[IOH]^2,$$

where E = total concentration of electrolytes and e = a variable factor depending on the concentration of I' and OH'.

Under special experimental conditions (when $OH'/I' < 10$), the member $e(E)$ of the equation becomes negligibly small, and the simpler formula

$$-\frac{d[IOH]}{dt} = \frac{[I']}{[OH']} \cdot [IOH]^2,$$

expresses the rate of change.

In the experiments which follow, the initial concentration of iodine ions and hydroxyl ions was twenty times greater than that of the hypoiodous acid, so that, despite the fact that hydroxyl ions

are used up and iodine ions formed during the reaction, the ratio [I']/[OH'] remained practically constant.

The method of procedure was as follows: Two hundred c.c. of a $N/50$-iodine solution (in potassium iodide) were rapidly mixed with an equal volume of $0.4N$-sodium hydroxide solution, so that the concentration of the mixture was (in mols. per litre)

$$0.005I_2 + 0.2NaOH + 0.2KI.$$
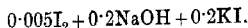
Successive quantities of this solution (20 c.c. each) were removed after the specified time; excess of phenol (3 c.c. of a 5 per cent. solution) was added to combine with the "active iodine," the mixture acidified with acetic acid, and the iodine thus liberated (from the iodate and iodide) was titrated with $N/10$-thiosulphate.

Two explanatory remarks are here needed:

(i) The reaction between phenol and "active iodine" in the presence of excess of the former is very rapid. This may be seen by simply adding phenol to a freshly prepared solution of iodine in alkali; the yellowish-green colour of the latter immediately disappears. The speed of the reaction was also proved by allowing phenol to act for various lengths of time (from 0.5 to 20 minutes) on solutions of equal "active iodine" content; the amount of iodine used up was the same, irrespective of the time allowed before acidifying.

(ii) It is essential that acetic acid or some other weak acid is employed for acidifying the mixture. If a strong mineral acid is used, then iodine is liberated from the iodate and iodide present before the whole of the hydroxyl ions have been neutralised; hypoiodous acid is consequently formed and acts on the phenol, causing an apparent increase in the amount of "active iodine." This phenomenon was first described by Kekulé, and its effect on the estimation of hypoiodous acid was later eliminated by saturating the solution with carbon dioxide before acidifying (Batey, *Analyst*, 1911, **38**, 132). If acetic acid is used, the treatment with carbon dioxide becomes unnecessary; this was proved by means of blank experiments on a mixture of sodium iodate and iodide in the presence of phenol.

In the table below, the third column gives the amount of "active iodine" in terms of c.c. of $N/100$-iodine solution; k_1, k_2, and k_3 are constants corresponding with reactions of the first, second, and third order respectively, that is,

$$k_1 = \frac{1}{t_2 - t_1} \cdot \log \cdot \frac{c_1}{c_2}; \; k_2 = \frac{c_1 - c_2}{(t_2 - t_1)c_1 c_2}; \; k_3 = \frac{1}{2(t_2 - t_1)} \cdot \frac{1}{c_2^2} - \frac{1}{c_1^2}$$

Table showing the Velocity of Decomposition of the "Active Iodine Compound" in Alkaline Solution.

Time.	C.c. of $N/100$-thiosulphate required.	$c=$ "active iodine."	10^2k_1	10^3k_2	10^4k_3
0	0	19·5	—	—	—
1 min.	2·0	17·5	4·20	5·8	3·15
2 ,,	3·7	15·8	4·43	6·14	3·65
3 ,,	5·0	14·5	3·73	5·67	3·8
5 ,,	7·4	12·1	4·43	6·84	5·35
8 ,,	10·1	9·4	3·66	7·90	7·5
10 ,,	11·3	8·2	2·96	7·78	8·9
14 ,,	13·0	6·5	2·52	7·96	11·0
18 ,,	14·1	5·4	2·01	7·83	13·4
25 ,,	15·2	4·3	1·41	6·80	14·1
30 ,,	15·8	3·7	1·30	7·53	19·0
40 ,,	16·5	3·0	0·91	6·31	19·1
60 ,,	17·3	2·2	0·67	6·01	23·8
90 ,,	18·7	1·5	0·53	7·07	39·7

Mean $10^3k_2=$ 6·90

The temperature of the solution remained approximately constant $(10·3—10·7°)$ throughout the experiment.

It will be seen from the foregoing table that whilst k_1 and k_3 vary considerably, k_2 remains satisfactorily constant over a wide range of concentration, thus proving the decomposition of the "active substance" to be a bimolecular reaction, just as is the case with hypoiodous acid; the occurrence of a maximum in the value of the constant is also suggestive of the decomposition of hypoiodous acid, and, finally, k_2 as above determined can be shown, after applying the necessary corrections, to have the same value as the constant obtained by other authors for the rate of decomposition of hypoiodous acid.

Thus, Skrabal (*Monatsh.*, 1911, **32**, 171), working at $20·2°$ with alkaline iodine–potassium iodide solutions of the same concentration as employed above, obtained for the constant of the rate of decomposition of hypoiodous acid (k'_2) the mean value $2·63 \times 10^3$. Two corrections are needed to make the constant found for the "active substance" comparable with that obtained by Skrabal, namely, (i) a correction for the difference in the amount of solution analysed, and (ii) a correction for the difference in the temperature.

(i) From the equation

$$k_2 = \frac{c_1 - c_2}{(t_2 - t_1)c_1c_2}$$

it is easily seen that k_2 is inversely proportional to the quantity of solution analysed at a time. As this was 89·49 c.c. in Skrabal's

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case, whilst the present author used only 19·5 c.c., the first correct-ing factor for the constant will be $\dfrac{19\cdot5}{89\cdot49}$.

(ii) The temperature-coefficient of the constant was found by Skrabal to be 2·1 (per 10°). Now, k_2 was determined at 10·5° and k'_2 at 20·2°, a difference of 9·7°, hence the second correcting factor for the constant is $\dfrac{2\cdot1 \times 9\cdot7}{10}$.

Applying these two corrections, we obtain

$$k_{2\text{(corrected)}} = 6\cdot90 \times \frac{19\cdot50}{89\cdot49} \times 2\cdot1 \times \frac{9\cdot7}{10} \times 10^3$$

$$= 3\cdot06 \times 10^3.$$

The agreement between the two constants is good, bearing in mind that the "mean value" (that is, the arithmetical mean) of the constants made use of in the above calculations is only a rough approximation to their true value.

Having thus proved that the iodine which combines with the phenol in alkaline solutions is present as hypoiodous acid, and having shown that there is strong evidence for assuming that the same compound is the active substance in iodine monochloride solutions, other methods used in the preparation of iodophenols may be examined. A close scrutiny will show that in most, if not all, the processes by which these compounds are obtained, hypo-iodous acid is an intermediate product.

(1) *"Iodine and Mercuric Oxide" Method.*—The formation of hypoiodous acid from these two substances in the presence of water is a matter of common knowledge (Köne, *Ann. Phys. Chem.*, 1845, [ii], **66**, 300; Taylor, *Chem. News*, 1897, **76**, 22).

(2) *"Hypochlorous Acid and Potassium Iodide" Method.*—The interaction between hypochlorous acid and potassium iodide, result-ing in the formation of hypoiodous acid, has been studied by Klimenko (*Zeitsch. physikal. Chem.*, 1897, **23**, 552, 558) and con-firmed by Bray (*ibid.*, 1906, **54**, 563). We may therefore sub-stitute for Dagener's complicated formula the following:

$$C_6H_4(OH)_2 + 3IOH = C_6HI_3(OH)_2 + 3H_2O.$$
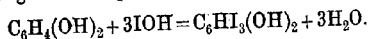
(3) *"Iodine and Iodic Acid" Method.*—The reaction

$$5IOH \rightleftharpoons 2I_2 + HIO_3 + 2H_2O$$
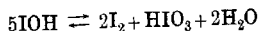
is a reversible one, and the continuous removal of hypoiodous acid by the phenol causes it to proceed towards the left.

(4) *"Iodine and Sodium Phosphate" Method.*—Iodine dissolves

in a solution of disodium hydrogen phosphate, the simplest way of formulating the reaction being

$$Na_2HPO_4 + I_2 + H_2O \rightleftharpoons NaH_2PO_4 + NaI + IOH \quad . \quad . \quad (i)$$
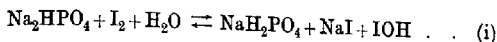
The hypoiodous acid thus formed decomposes further,

$$5IOH \rightleftharpoons HIO_3 + 2I_2 + H_2O \quad . \quad . \quad . \quad . \quad (ii)$$
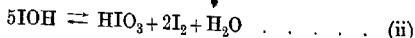
so that, finally, hypoiodous acid is in equilibrium on the one hand with iodine and sodium phosphate, and on the other with iodine and iodic acid. The following experiment confirms this view.

A solution of iodine and disodium hydrogen phosphate in water was prepared and allowed to remain for a fortnight, so that equilibrium was attained; the solution was still of a red colour, showing that free iodine (or, more correctly, I'_3) was present. To one portion of this solution phenol was added, which combined with the "active iodine" and decolorised the solution; the mixture was then immediately acidified, and the iodine liberated from the iodide and iodate present was titrated with $N/100$-thiosulphate. Another portion of the same solution, after adding phenol, was allowed to remain for twenty-four hours before acidifying and titrating as above. The amount of iodine used by the phenol was in both cases the same. This is exactly what is to be expected from the equations put forward above; the addition of phenol removes the hypoiodous acid present, thus disturbing both equilibria, but, since reaction (i) has a far greater velocity than reaction (ii), practically the whole of the free iodine combines with the sodium phosphate, leaving the iodate ion unaffected.

The reaction between iodine and disodium hydrogen phosphate is formulated in a rather different way by Skrabal and Gruber (*Monatsh.*, 1916, **37**, 543), who give the equation

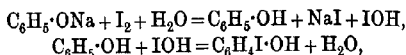$$3I_2 + 6HPO''_4 + 3H_2O = 5I' + IO'_3 + 6H_2PO'_4,$$
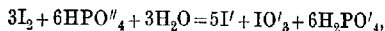
but it is obvious from the result of the above experiment that this equation does not represent the actual state of affairs; for, if it did, since the reaction is a balanced one, the removal of the free iodine by the phenol (supposing this to be possible without the intermediate formation of hypoiodous acid) would cause the reaction to proceed towards the left until no more iodate ion remained in solution. This, however, is not the case, for, as we have seen, the iodate remains unaffected by the removal of the "active iodine."

(5) *Nitrogen Iodide Method.*—Selivanov (*loc. cit.*) proved that this compound yielded hypoiodous acid on hydrolysis, and sug-
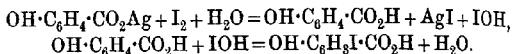
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gested that the iodination is due to the last-mentioned substance. He gave the following equations:

$$NI_3 + 3H_2O = NH_3 + 3IOH,$$
$$3IOH + 3C_6H_5 \cdot OH = 3C_6H_4I \cdot OH + 3H_2O.$$
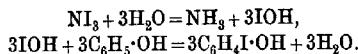
(6) Passing on to the "dry" reactions of Birnbaum and Schall, we see that even here the formation of hypoiodous acid is not excluded. A very small quantity of moisture would be sufficient, since the water used up in the first part of the reaction is regenerated at the end. Thus in Schall's method

$$C_6H_5 \cdot ONa + I_2 + H_2O = C_6H_5 \cdot OH + NaI + IOH,$$
$$C_6H_5 \cdot OH + IOH = C_6H_4I \cdot OH + H_2O,$$

and in Birnbaum's

$$OH \cdot C_6H_4 \cdot CO_2Ag + I_2 + H_2O = OH \cdot C_6H_4 \cdot CO_2H + AgI + IOH,$$
$$OH \cdot C_6H_4 \cdot CO_2H + IOH = OH \cdot C_6H_3I \cdot CO_2H + H_2O.$$

This new way of formulating the reactions obviates the necessity of assuming any intramolecular change. It should be further noted that Kekulé's criticism of Lautemann's method applies also to the last-mentioned reaction; in all probability, the formation of iodo-salicylic acid does not take place on heating iodine with silver salicylate, but during the subsequent treatment. In any case, the preliminary heating is quite superfluous; if to a suspension of silver salicylate in alcohol is added a solution of iodine (in alcohol), the colour of the latter disappears quickly at first, the reaction becoming slower as the ratio between silver salicylate and iodine added approaches unity. After removing excess of iodine by shaking with mercury and filtering, there is obtained, on evaporating the alcohol, a mixture of iodosalicylic acids.

The theory that the formation of iodophenols is due to the action of hypoiodous acid is thus seen to explain the preparation of those compounds by many different methods. The real test for a useful theory, however, is its capability of predicting new pheno-mena and suggesting fresh lines of research. It will be seen that the above theory stands this test.

(i) For instance, it is evident that on the above theory any method of obtaining hypoiodous acid could also be used for the preparation of iodophenols; thus, it can be predicted that iodo-phenols will be formed by the action of silver carbonate or sulphate and iodine on phenols.

(ii) The converse proposition, that any method of preparing iodophenols may be made to yield hypoiodous acid, is probably

also true. This has been shown to be the case in the iodine and sodium phosphate method of Richard.

(iii) A further successful line of research suggested by the present theory, namely, the estimation of hypoiodous acid, will be dealt with in a later paper.

So far, the hypoiodous theory of iodination has been applied to phenolic compounds only, but many of the methods for the preparation of iodophenols, such as Kekulé's (iodine and iodic acid) and Weselsky's (iodine and mercuric oxide), have been successfully used in introducing iodine atoms into other organic compounds. Again, the formation of iodoform from alcohol and from acetone has been proved to be due to hypoiodous acid (Daventer and van't Hoff, *Rec. trav. chim.*, 1888, **1**, 35; Pieroni, *Gazzetta*, 1912, **42**, i, 534). It will be seen from this that hypoiodous acid as an iodinating agent has a much wider range than that outlined above. Its formation might possibly explain the action of concentrated sulphuric and nitric acids, ferric chloride, etc., as iodine carriers (Neumann, *Annalen*, 1887, **241**, 84; Meyer and Schwalb, *ibid.*, 1885, **231**, 195; Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1917, **39**, 441).

Throughout this paper, the term "hypoiodous acid" has been employed to denote the compound IOH, although, so far as its properties are concerned, "iodine hydroxide" would be a more suitable term. The latter name has been avoided, as it suggests the existence of positive iodine ions, which many chemists regard with suspicion. The work of Walden (*Zeitsch. physikal. Chem.*, 1903, **43**, 385) on the conductivity of iodine in inorganic solvents, as well as other considerations (Abegg and Auerbach, "Handbuch d. anorg. Chem.," IV, (ii), 455), lend, nevertheless, considerable support to the view that iodine cations do exist. If this be really the case, then the previous statement may be modified to: the formation of iodophenols, and that of hypoiodous acid, is brought about by the presence of positive iodine ions.

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XC.—The Influence of Hydrogen Sulphide on the Occlusion of Hydrogen by Palladium.

By Edward Bradford Maxted.

The activation of hydrogen by metallic catalysts is undoubtedly intimately connected with the phenomenon of occlusion; indeed, hydrogenation reactions which proceed in the presence, for instance, of palladium and free hydrogen, may also be effected by palladium containing hydrogen in the occluded state.

From this point of view the factors that determine the catalytic activity of various preparations of a given metal for hydrogenation reactions should include the occlusive power of the preparation for hydrogen, and it should follow, as a necessary sequence, that substances which exert an inhibitive effect on catalytic activity will also inhibit the occlusive power.

For the purpose of the present paper, hydrogen sulphide has been taken as a typical catalyst poison, palladium being chosen as the occluding material by reason of its high absorptive power for hydrogen.

It may be mentioned, with reference to the influence of other catalytically poisonous substances on the occluding power of palladium for hydrogen, that De Hemptinne (*Zeitsch. physikal. Chem.*, 1898, **27**, 249) noticed that palladium which had been treated with carbon monoxide lost its absorptive power for hydrogen, at any rate at low temperatures. Carbon monoxide was afterwards found by Paal and Hartmann (*Ber.*, 1910, **43**, 243) to inhibit the activity of this metal for the catalytic reduction of sodium picrate. The latter authors, together with Steyer (Paal and Hartmann, *Ber.*, 1918, **51**, 711; Paal and Steyer, *ibid.*, 1743), showed also that mercury acts similarly on palladium hydrosols.

In the work about to be described the hydrogen-occluding power of oxygen-free palladium-black was measured before and after treatment with hydrogen sulphide, and, incidentally, data were obtained relating to the absorption of hydrogen sulphide by palladium and the stability of the absorption compound.

Experimental.

The apparatus employed consisted of a small glass absorption pipette containing a known weight of palladium-black and connected by means of capillary glass tubing to a Sprengel pump and

to a gas burette respectively. This gas burette, which contained mercury, was provided with a three-way cock for the introduction of gas. The various parts of the apparatus were joined by fusion, and all stopcocks were mercury-sealed. In order to prevent access of mercury vapour to the palladium, short plugs of aluminium turnings, preceded and followed by glass-wool, were inserted in the system on each side of the absorption pipette.

The palladium was prepared in the apparatus itself by the reduction of palladium chloride at 100° by means of electrolytic hydrogen, from which the last traces of oxygen had been removed by treatment with palladinised asbestos at 350°, followed by soda-lime.

According to the measurements of Mond, Ramsay, and Shields (*Proc. Roy. Soc.*, 1897, [*A*], **62**, 290), palladium-black occludes about 873 volumes of hydrogen at the ordinary temperature and pressure. The ease and rapidity with which this is given up varies somewhat with the nature of the palladium, but, in any case, the bulk is evolved in a vacuum at 100°. The greater part of the hydrogen occluded is taken up at once, but a slight additional absorption takes place on allowing the palladium to remain in hydrogen.

In order to avoid the possibility of changing the nature, and especially the catalytic activity, of the palladium-black by overheating, it was decided, in the present case, to regard 100° as the maximum temperature to which the palladium should be subjected, this temperature being, as already stated, sufficiently high for the extraction by exhaustion of practically the whole of the occluded hydrogen.

The first point to be studied was the constancy of the volume of hydrogen which could be removed by exhaustion at 100° or, alternatively, occluded by exposing palladium, which had been dehydrogenated in this way, to the action of fresh hydrogen at the ordinary temperature. In order to ensure uniformity in the experimental conditions, the system was in every case exhausted to a standard pressure of 3 mm. at 100°, and exhaustion was continued as long as any appreciable quantity of gas was being evolved under these conditions, the hydrogen being collected over mercury in the usual way. Subsequently, a known volume of hydrogen was admitted to the absorption tube from the gas burette and the contraction read off, the volume of the absorption pipette, including its connexions, having been determined previously.

Table I summarises the results of eight experiments carried out in this way. The measurements numbered 5 and 6, also those numbered 7 and 8, were made with fresh quantities of palladium-black, which in every case weighed 0·6 gram, corresponding with

1 gram of palladium chloride. The volume of gas evolved or occluded is in every case reduced to normal temperature and pressure.

TABLE I.

No. of expt.	Vol. of hydrogen evolved on exhaustion. C.c.	Vol. of hydrogen subsequently occluded. C.c.
1	41·3	40·0
2	40·2	40·5
3	41·9	41·1
4	41·4	—
5	41·5	40·6
6	41·9	—
7	41·6	40·5
8	41·5	—

The average volume of hydrogen evolved or occluded under the above conditions is thus about 41 c.c., corresponding with 68·5 c.c. per gram of palladium.

Dry hydrogen sulphide, prepared by the action of heat on a solution of magnesium hydrosulphide, was now allowed to pass into the exhausted reaction tube in place of hydrogen and to remain in contact with the palladium, from which the occluded hydrogen had previously been removed by exhaustion at 100°. Occlusion of a certain amount of the gas took place at once, and was followed by a slower and continuous absorption of a secondary nature. It had previously been ascertained that hydrogen sulphide, provided it is dry and free from oxygen, does not attack either mercury or aluminium at a rate sufficient to influence the measurements.

Table II summarises an absorption experiment with 0·6 gram of palladium.

TABLE II.

Time.	Vol. H_2S absorbed. C.c. at N.T.P.
1 min.	6·2
5 min.	7·1
10 ,,	7·5
3 hr. 20 min.	10·4
18 hr.	12·2
40 ,,	13·5

By interrupting the absorption after a suitable time of contact, palladium containing various proportions of hydrogen sulphide could be obtained. The hydrogen sulphide thus absorbed was not removed to any great extent by exhaustion at the ordinary temperature, this being especially the case when the hydrogen sulphide content of the palladium was comparatively low, and, on passing hydrogen into the

exhausted absorption pipette, occlusion of this gas no longer took place.

Under the conditions employed, it was not found possible, in view of the velocity of the primary occlusion of hydrogen sulphide by palladium, to prepare specimens of the metal containing less than about 13·5 c.c. of hydrogen sulphide per gram, corresponding with an absorption of about 8 c.c. for the 0·6 gram of palladium taken for each experiment, and the minimum volume of hydrogen sulphide required for the total inhibition of the hydrogen-occluding properties of palladium could therefore not be determined. This figure is, however, certainly less than 14 c.c. per gram of palladium.

On exhausting the palladium containing hydrogen sulphide at 100° a volume of gas, approximately equal to that of the hydrogen sulphide contained in the preparation, was evolved, but was found on analysis to consist almost entirely of hydrogen, the sulphur of the absorbed gas being retained by the palladium.

Table III records three results of this nature.

TABLE III.

No. of expt.	Wt. of Pd in grams.	Vol. of H_2S absorbed.	Occlusive power for hydrogen.	Vol. of gas evolved in a vacuum at 15°.	Vol. of gas subsequently evolved in a vacuum at 100°.	Analysis of total gas evolved	
						H_2. C.c.	H_2S. C.c.
1	0·6	8·2	Nil.	0·1	8·2	8·3	—
2	0·6	13·5	,,	1·1	12·8	13·7	0·2
3	0·6	17·7	,,	2·3	16·4	17·4	1·3

An interesting observation was made with respect to the specific influence of the nature of the sulphur absorption compound on the occlusive power of the palladium for hydrogen, in that, whilst about 8 c.c. of hydrogen sulphide are sufficient to inhibit completely the occlusive power for hydrogen of 0·6 gram of palladium, the equivalent quantity of sulphur, which remains behind after exhaustion at 100°, is by no means sufficient to prevent completely the occlusion of hydrogen.

In order to study quantitatively the influence of sulphur in the latter form, measurements were made of the volume of hydrogen which was capable of being absorbed or evolved by various specimens of palladium of known sulphur content, the hydrogen portion of the absorbed hydrogen sulphide having been previously extracted by exhaustion at 100°.

The results obtained are tabulated below, the measurements of occlusive power having been carried out under similar conditions to

the experiments recorded in table I.   The sulphur content was deter-
mined both by measuring the volume of hydrogen sulphide which
had been absorbed, subtracting any small quantity evolved as such
during the preliminary exhaustion at 100°, and also, as a check, after
measuring its occlusive power, by dissolving the preparation in aqua
regia and precipitating as barium sulphate.   In order to obtain a
preparation containing as high a proportion of sulphur as 0·0328
gram to 0·54 gram of palladium, corresponding with an absorption
of 23·0 c.c. of hydrogen sulphide, an absorption period of about
three weeks was necessary.

Sulphur content in milligrams.

TABLE IV.
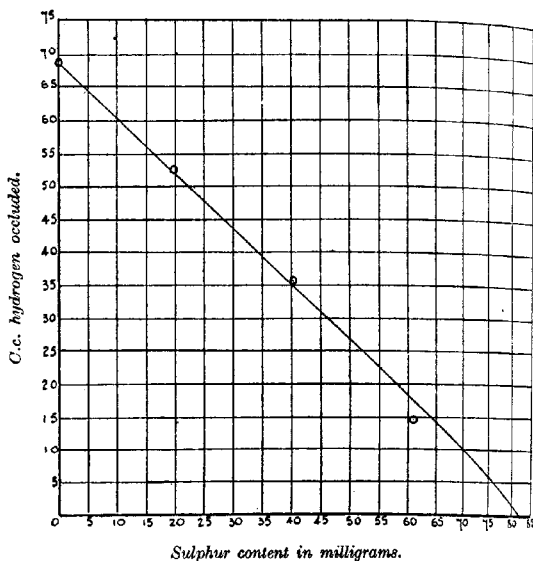
| | | | Occlusive power for hydrogen. | |
No. of expt.	Wt. of Pd. Gram.	Wt. of sulphur content. Gram.	Vol. absorbed. C.c. at N.T.P.	Vol. subsequently evolved. C.c. at N.T.P.
1	0·6	0·0117	31·7	31·6
2	0·6	0·0117	31·8	32·4
3	0·6	0·0117	31·3	31·0
4	0·6	0·0117	30·7	—
5	0·6	0·0242	21·2	21·6
6	0·54	0·0328	8·4	8·2
7	0·54	0·0328	8·0	7·9
8	0·54	0·0328	7·7	7·9

On plotting the above results graphically, it will be seen that the mean occlusive power for hydrogen is approximately a linear function of the sulphur content, and that each atom of sulphur renders almost exactly four palladium atoms incapable of occluding hydrogen, the remainder of the palladium being capable of occluding normally. The accompanying curve, which shows this relation, refers to 1 gram of palladium.

Whilst any discussion respecting the constitution of the compound formed by the decomposition of hydrogen sulphide by palladium does not fall within the scope of the present paper, it may be noted that the occlusive power of a preparation of this kind may be predicted by assuming a compound Pd_4S to be formed, and ascribing to the residual palladium its normal power of absorption. There is, however, insufficient evidence to justify the assumption of the actual formation of this or any compound, and it may be mentioned in this connexion that palladium foil was found to remain untarnished by pure dry hydrogen sulphide both at the ordinary temperature and at 100°.

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WALSALL, STAFFS.   [Received, July 10th, 1919.]

XCI.—The Critical Solution Temperature of a Ternary Mixture as a Criterion of Purity of Toluene.

By KENNEDY JOSEPH PREVITÉ ORTON and DAVID CHARLES JONES.

THE use of binary critical solution temperatures in the determination of purity has become well known since Crismer (Bull. Soc. chim. Belg., 1895, 9, 145; 1896, 10, 312; 1904, 18, 1; 1906, 20, 294) originally demonstrated the great delicacy of the critical solution temperature of the alcohol–petroleum binary in detecting the presence of, and in estimating the amount of, water in the alcohol. As a means of distinguishing rapidly between various fats and oils and of testing the purity of liquid substances, the use of critical points has been considerably developed. The occurrence, however, of the critical points of binary mixtures in convenient ranges of temperature is relatively rare, and hence the applicability of the method is for practical purposes comparatively limited.

This disadvantage largely disappears in a ternary mixture. If

will sufficiently illustrate the effect of various substances which we have examined.

The solubility of paraffin hydrocarbons in acetic acid and in water is very much less than that of toluene. The presence of petroleum raises, therefore, the c.s.t. of the systems toluene–acetic

FIG. 1.
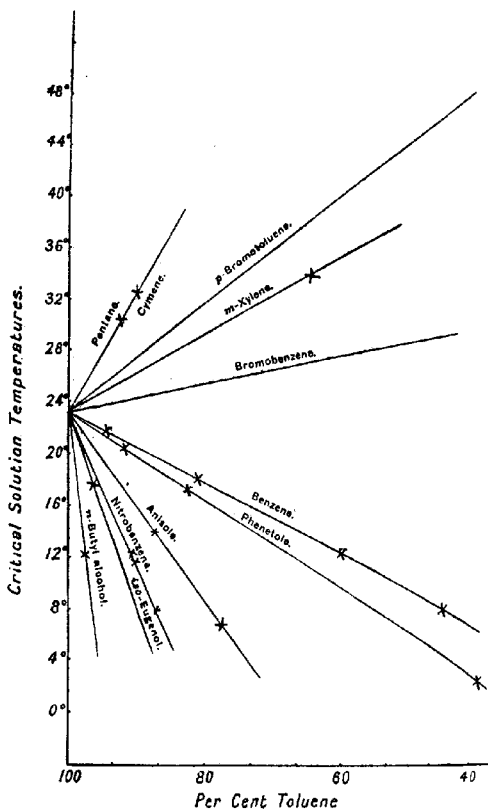
acid–water and benzene–acetic acid–water in a very marked way. If the toluene contains 1 per cent. of petroleum (b. p. 124—132°, octane), the c.s.t. (23·5°) is raised by 1·6°. Since the temperature of critical solution can be read with certainty to 0·1° at the range of temperature used, such small proportions as one-sixteenth per

cent. of paraffin can be detected in benzene, toluene, xylene, and the like, and the proportion estimated to the same degree of accuracy. For paraffin in benzene, the method is far more delicate than the melting point. The fact that the same aqueous acetic acid can be used in the three hydrocarbons named is an additional advantage.

In the homologous series of paraffin hydrocarbons, the solubilities are very similar, but the progressive decrease of solubility as the series is ascended in the effect on the c.s.t. of the toluene–acetic acid–water system is obvious (table II).

TABLE II.

Substance present as impurity in toluene.	Elevation or depression of c.s.t. for 1 per cent. of substance.
Benzene	−0·27°
Xylene	0·29°
Cymene	0·90°
Pentane	0·90°
Hydrocarbon fractions mainly b. p. 109–110°	1·4°
(Octane) 124–132°	1·6°

If it be assumed that the complete substitution of octane for toluene is accompanied by a proportional rise in the c.s.t., the c.s.t. of pure octane with this particular aqueous acetic acid will be about 160°. Since increase in the concentration of the acetic acid solution used lowers the temperature of critical solution, it appears probable that some paraffin hydrocarbons would give binary critical solution temperatures with more concentrated—glacial—acetic acid. We have determined (approximately) the values of certain fractions.

TABLE III.

				c.s.t.
Hexane.	Acetic acid, m. p. 15·6°			1°
Hexane.	„ „ 15·0°			25°
Hydrocarbons boiling at 205–225°				59°
„ „ 225–240°	Acetic acid, m. p. 16·15°		66·5°
„ „ 240–264°			81·0°

This similarity in solubility relation among the homologous fatty paraffins, which is the cause of this small difference in the values of the c.s.t., may be contrasted with the widely varying relations among the fatty acids.

In Fig. 2 (in which we have followed Roozeboom, " Heterogene Gleichgewicht," Vol. III.), $CC_1C_2C_4C_5$ represents the critical curve of the system toluene–acetic acid–water from the binary c.s.t. of

toluene–water, C (which we find to lie approximately at $250°$, under pressure), through the ternary c.s.t.'s on the isothermal binodal curves; the base of the prism corresponds with an isothermal just below $0°$. Similarly, $C'C'_1C'_2C'_3C'_4C'_5$ represents the corresponding critical curve for benzene. In the enlarged inset (X), K and K' represent the ternary c.s.t.'s of the toluene and benzene systems, respectively, at the isothermal $23·5°$, whilst K_1 and K'_1 represent the c.s.t.'s at $-3·3°$.

FIG. 2.
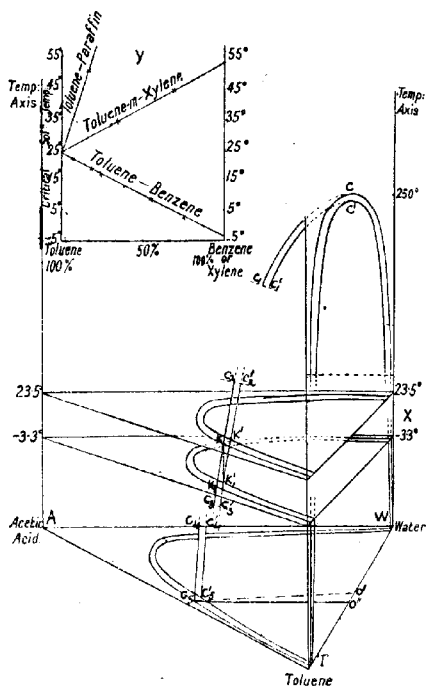
The percentage composition of the system at K is: toluene, $39·34$; acetic acid, $54·52$; water, $6·14$.

The percentage composition of the system at K'_1 is: benzene, $39·72$; acetic acid, $54·22$; water, $6·06$.

Waddell's values for the benzene system at $25°$ are: benzene, $39·6$; acetic acid, $54·22$; water, $7·6$.

If in a system the composition of which is represented by K the

toluene is gradually displaced by the same volume of benzene, the critical phenomenon exhibited by the system remains always distinct up to the complete replacement of toluene, that is, KK'_1, a line parallel to the temperature axis, cannot be detected as having left the region of the critical curve. The great similarity in the solubility relations of benzene and toluene would account for this behaviour. Moreover, the temperature of the (now) quaternary c.s.t. is linearly related to the increasing proportion of benzene in the system (inset Y, Fig. 2). Quite analogous results were found to hold in the case of xylene, the critical curve being as much without that of toluene as that of benzene within, and also, as the diagram (Y) shows, replacement of toluene by xylene causes a linear corresponding alteration in the c.s.t.

On the other hand, the critical curves of aqueous acetic acid–petroleum and aqueous acetic acid–toluene, owing to the greater difference in solubility, lie very much further apart. It is probable that in cases of this kind, substitution of petroleum for toluene would lead the system away from the curve, but up to 17 per cent. of petroleum the critical phenomena remain very distinct, and the relation between the proportion of petroleum and the elevation of the c.s.t. is linear (Fig. 6).

Relation between Melting Point of the Acetic Acid and the c.s.t. with Toluene.

The c.s.t. of the ternary system toluene–acetic acid–water rises proportionally to the increase in the quantity of water over a small range—3·5 per cent. and the elevation of the c.s.t. is almost linearly related to the depression of melting point of the acetic acid (Table IV, and Fig. 3.)

FIG. 3.

TABLE IV.

M.p. of aqueous acetic acid.	Percentage of water.	c.s.t.
5·45°	8·2	−5·9°
4·2°	9·0	9·8°
2·77°	10·1	23·5°
0·9°	11·7	41·9°

(The percentage of water is obtained from Faucon's numbers, *Ann. Chim. Phys.*, 1910, [viii], **19**, 84).

Similarly, the c.s.t. of the binary system alcohol–petroleum (Crismer) and benzene–formic acid (Ewins) rises proportionally to the concentration of water added.

Melting Points of Acetic Acid
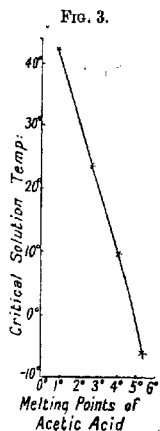
In Fig. 2, let C_5 represent the critical point on the lowest binodal curve, ATW; on replacing acetic acid by water, keeping the proportion of toluene constant, the composition of the system follows the line CO'' parallel to the acetic acid–water line, AW. CO', the projection of the critical curve on the isothermal plane, represents the whole series of critical compositions up to the binary c.s.t. of toluene and water. Hence, unless O' approximates to O'' in position (assuming CO' to be a straight line), addition of water soon takes the system away from the region of the critical curve. The phenomenon of critical solution, then, will not appear when the temperature of miscibility is observed. It must be emphasised that in our experiments the distance travelled by the system as water replaces acetic acid, along CO'', is relatively very small. The system is still found sufficiently near to the critical curve for an obvious exhibition of the critical phenomena.

Measurement of the Constituents.—In using the change in the c.s.t. of a ternary mixture produced by an impurity for the purpose of estimating the impurity, such as we are suggesting, accuracy of measurement of the quantity of the constituents is of the greatest importance (compare Timmermans, *loc. cit.*). Thus, as an illustration, the numbers given in the table of the temperature of the critical solution of the system toluene–acetic acid–water show the effect of an increase in the proportion of toluene (pure) of less than 1 per cent.

TABLE V.

Aqueous acetic acid.	Toluene.	Difference.	c.s.t.	Difference.
0·6232	0·5006	0·0144	24·05°	1·65°
0·6232	0·4862	0·0144	22·4°	

The difference 1·65° would correspond with the presence of 1 per cent. of petroleum.

In the figure (2), the point K'_1 represents the composition of the ternary c.s.t. of benzene–acetic acid–water. Any change in the proportion of any one constituent causes the composition of the system to move either into a region of heterogeneity within the binodal curve or of unsaturation and homogeneity without the curve. In systems such as benzene–acetic acid–water (or toluene–acetic acid–water), the solubility relations of which change slowly with alteration of temperature, a considerable temperature change would be required before the miscibility point of the new system is reached. In other words, the sensitiveness of the c.s.t. to slight variations in composition is a consequence of the great extension of the figure along the temperature axis.

The very great importance of accuracy of proportions of the

constituents in a binary as well as in a ternary mixture is well illustrated by a perhaps extreme case which we have observed. Fig. 4 shows the effect of addition of toluene to two mixtures of *n*-butyric acid and water, one containing 41 and the other 33 per cent. of the acid.   These two mixtures both give the same miscibility temperature ($-3.7°$) in the critical region, owing to the long, flat top of the solubility curve (Faucon, Rothmund, *Zeitsch. physikal. Chem.*, 1908, **63**, 57, and Timmermans). The solubility curve of the system alcohol–petroleum has a similar form.

If one regards the toluene as an impurity in the binary system butyric acid–water, each curve (Fig. 4) may be taken to show the effect of increasing concentration of the impurity on the binary c.s.t.

If, however, it is desired to estimate by the elevation of the c.s.t the proportion of impurity, it will be seen that it is obviously essential that the proportions in which the constituents are taken shall be exactly known. If the proportion of *n*-butyric acid is 41 per cent., then the presence of 1 per cent. of toluene causes a rise in the c.s.t. of $21°$ (Fig. 4), whereas if the proportion of *n*-butyric acid is 33 per cent., 1 per cent. of toluene gives a rise of $35°$.

FIG. 4.

Critical Solution Temperature

Alternatively, let the concentration of toluene be fixed at 1 per cent., then a variation of the proportion of butyric acid from 41 to 33 per cent. will lead to a change in the c.s.t. of $15°$. Yet in the absence of toluene both acid–water mixtures will have the same miscibility temperature.

This example brings out very clearly the necessity of using exact proportions of the constituents when the binary c.s.t. is being used as a criterion of the degree of purity.   Only when the liquid is finally purified are the exact proportions of less importance, since before that stage is reached the system is not binary, but of a higher order.   Thus, in the use which is commonly made of the alcohol–petroleum binary to *estimate* the proportion of water in the alcohol, it is essential, even for small quantities of water, that certain definite proportions of petroleum and aqueous alcohol should be used.
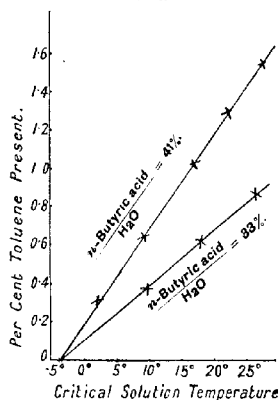
It is obviously of first importance, if the method is to become of practical utility, that the proper degree of accuracy should be combined with rapidity and simplicity of manipulation. We find that a remarkably high degree of accuracy can be reached by using small, carefully constructed pipettes, one for the solution of fixed concentration and the other for the liquid the purity of which is to be tested. The manipulation and the method of estimating petroleum in toluene which we recommend have been tested in the analytical laboratory of a large chemical works, and have received a very favourable report as giving accurate and consistent results in the hands of the average manipulator.

<div align="center">EXPERIMENTAL.</div>

Apparatus.—The accurate measurement of (1) the solution used, (2) the liquid the purity of which is to be tested, is the first consideration in using this method. Weighing of liquids is a lengthy and difficult operation. We find that for small volumes the degree of accuracy which can be reached with properly constructed pipettes is quite remarkable. The diagram (Fig. 5) shows the form and the dimensions of the pipettes we have used. The essentials in the form and use of the pipettes are as follows: (1) The tip of the pipette is drawn into a fine capillary tube, so that the liquid may be held with certainty to the mark, whilst the time for delivery is about one minute for volumes 0·5—1 c.c. (2) The stem of the pipette should be of small diameter, since with wide tubes, (*a*) change in pressure of the finger causes a very appreciable variation in the height of the meniscus, an effect which is very marked with a pipette having an ordinary tip; (*b*) error in adjustment of the meniscus is magnified. (3) After drawing in a liquid and adjusting to the mark, the outside of the tip should be gently wiped with a silk duster, at the end of which operation the liquid fills the pipette from the mark to the end of the tip. (4) When the pipette has ceased delivering, the capillary tip (in contact with the glass) is emptied by a gentle blow. (5) Every care is taken to have a clean glass surface; finally, the pipette is washed out with distilled water and dried by a current of dust-free air.

The following illustrations will emphasise the extremely small error entailed in the use of these pipettes. A "5 c.c." pipette, terminating in a fine capillary tube, delivered its content of water in two minutes. At a definite temperature, it delivered in five successive trials 4·95979 c.c., 4·95986 c.c., 4·95995 c.c., 4·95966 c.c., 4·96011 c.c.; the volumes are calculated from the weights of water delivered. It will be seen that the maximum variation between

any two readings is 0·00045 c.c., and the maximum variation from the arithmetic mean 0·00024 c.c., or 0·005 per cent.

A "2 c.c." pipette, which delivered its content of water in only ten seconds, lengthened, however, in delivery to one minute, gave the following weights of water in five successive experiments: 2·0146, 2·0146, 2·0172, 2·0138, 2·0172 grams. Here the maximum variation reaches 0·0034 gram, and from the arithmetic mean is 0·0017 gram, or 0·08 per cent.

A very small pipette, of the same type, but smaller than those we have generally used, delivering its content of water very slowly—in about one minute— gave the following readings in four successive experiments: 0·2524 c.c., 0·2524 c.c., 0·2525 c.c., 0·2527 c.c. The maximum variation between any two readings is 0·0003 c.c., and from the arithmetic mean 0·0002 c.c., or 0·1 per cent.

We have used small pipettes of various content, but for the apparatus in which we have observed the c.s.t. of the toluene-aqueous acetic acid and similar systems, pipettes of from 0·4 to 0·7 c.c. capacity are required. The aqueous acetic acid pipette delivered 0·6232 c.c., and the toluene pipette 0·4958 c.c. These are the quantities of our aqueous acetic acid (see later) and pure toluene, which we found to exhibit the phenomena of critical solution in the clearest and most obvious way. The maximum variation from the mean is 0·0002 c.c., and hence in one pipette the maximum error may amount to 0·03 per cent., and in the other to 0·04 per cent. An error of measurement of 0·001 c.c., that is, five times the actual maximum variation observed, produces a difference of 0·1° in the c.s.t. of toluene, and would correspond with an error of 0·0125 per cent. in the estimation of paraffin.

The experimental tube has the form and dimensions shown in the diagram (Fig. 5). The cap (A) is fastened on the tube (B) by a short piece of rubber tubing. This tube is attached to the

FIG. 5.
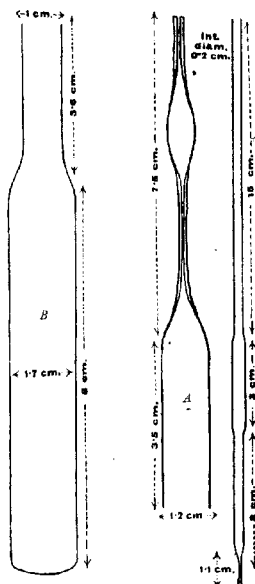
thermometer by rubber rings, and the whole combination is used as a stirrer of the bath.

The thermometer is a standard instrument, preferably graduated in twentieths, but a graduation in tenths will suffice for most purposes.

The bath is a glass beaker of ·2 litres capacity filled with water and heated by a small gas burner of the Argand type. The flame is simply and effectively regulated by a screw clip compressing a rubber tubing; the adjustment is very delicate when the rubber and slip are made fast to the bench, and hence the temperature is raised with the deliberation necessary as the temperature of critical solution is attained.

Determination of c.s.t.—At the ordinary temperature, the contents of the experimental tube are in two layers, the lower layer being mainly composed of aqueous acetic acid. As the temperature rises, the mutual solubility of the two layers increases, and they intermingle more readily as their densities, viscosities, etc., approach the same value, the suspensions of one layer in the other taking place in smaller drops requiring longer to separate. Gradually, striations appear through the body of the liquid, which is now distinctly opalescent. The temperature of the bath should now be rising at the approximate rate of 1° in five minutes. The striations become more and more delicate as the layers approach identity in every respect, and faint beginnings of blue fluorescence appear. This fluorescence deepens in tone, and when evident throughout the liquid, the striations being still clearly visible, the temperature of the bath must be raised more slowly at the approximate rate of 0·1° per minute. Close observation will now show the disappearance of the striations and greatly increased fluorescence. This temperature is taken as the critical solution point. The clearness with which one can see the thermometer scale through the liquid is a good test (first mentioned by Rothmund, *loc. cit.*) for observation in these final stages. The reading can now be repeated by cooling the bath very slightly, say 0·2°, and again taking the critical solution temperature. Readings may be repeated as often as desirable with the same mixture.

Materials.—The pure acetic acid was fractionated through an eight-bulb still-head. A considerable quantity was placed in a special double-stoppered bottle, and water added to bring it to the composition desired. We have used two solutions containing approximately 10·1 and 11·7 per cent. of water, and melting approximately at 2·77° and 0·9° respectively. To obtain a correct reading of the melting points of such dilute acetic acids is a very difficult matter (compare Faucon, *loc. cit.*). The temperature

cannot be determined within 0.02—$0.03°$. The acid melting at "$2.77°$" gave a c.s.t. with pure toluene at $23.5°$, and that melting at "$0.9°$" a c.s.t. at $41.9°$. A difference in melting point of $0.01°$ of the acetic acid leads to a difference of the c.s.t. with pure toluene of $0.1°$.

Since pure toluene can be readily obtained in quantity, it is better to prepare an aqueous acetic acid approximately of the desired composition, and then to determine the c.s.t. with pure toluene, rather than deduce the c.s.t. of the system from the melting point of the aqueous acetic acid.

Pure Toluene.—A quantity of toluene which had been prepared in the usual way from recrystallised toluene-p-sulphonic acid was shaken with saturated sodium carbonate solution, washed with distilled water twice, and dried over granulated calcium chloride (which does not, however, reduce the saturation point below $0°$ unless the liquid is simultaneously cooled). It was then fractionated through an eight-bulb still-head, and the large middle fraction refractionated. The "standard" toluene thus obtained has the characteristic that, on distillation, the first 10 c.c., the main fraction, and the last 10 c.c. yield the same c.s.t. with a given aqueous acetic acid. No change in the c.s.t. of the standard toluene could be observed after treatment with phosphoric oxide and refractionation.

The toluene has $D_{12.6}^{12.6}$ 0.87417; Perkin (T., 1896, **69**, 1241) gives $D_{12.6}^{12.6}$ 0.87403.

Benzene.—The benzene was obtained by fractionating a specimen (m. p. $5.4°$) until the fractions (first, main, and final) gave a constant c.s.t. with the standard "acetic" acid melting at "$0.9°$," when quantities identical with those taken for toluene were used. The value of the c.s.t. is $14.3°$. With acetic acid melting at "$2.77°$" the c.s.t. is $-3.3°$.

The Presence of Paraffin Hydrocarbons in Toluene.

For the purpose of studying the effect of the presence of paraffin hydrocarbons in toluene, the paraffin was obtained from American petroleum.

After shaking with sulphuric acid (95 per cent.) (which removes the olefines, Colman and Yeoman, *J. Soc. Chem. Ind.*, 1919, **38**, 57; Thole, *ibid.*, 39) until a fresh quantity of sulphuric acid remained uncoloured, the hydrocarbon was warmed and shaken with a mixture of nitric and sulphuric acids for many hours.

After washing with aqueous alkali and then with water, and drying with granular calcium chloride, it was distilled through an

eight-bulb still-head. After several fractionations, the two frac-tions, b. p. 109—110° and b. p. 124—132°, were used for admixture with toluene.

In determining the c.s.t. of the mixture, the pipette delivering 0·6232 c.c. was used for the aqueous acetic acid, and the pipette delivering 0·4958 c.c. for the mixture of toluene and petroleum. The results are summarised in the following table (VI) and graphically shown in Fig. 6.

TABLE VI.

A. Paraffin boiling at 124—132°. Aqueous acetic acid melting at "0·9°" and containing about 11·7 per cent. of water (Fig. 6).

Paraffin. Per cent.	c.s.t.	Paraffin. Per cent.	c.s.t.
0·0	41·8°	8·98	56·05°
1·054	43·65°	10·17	57·6°
1·31	43·9°	14·45	64·2°
2·08	45·4°	17·17	68·5°
3·926	48·1°		
6·17	51·4°		

B. Paraffin boiling at 109—110°. Aqueous acetic acid melting at "0·9°" and containing about 11·7 per cent. of water (Fig. 6).

Paraffin. Per cent.	c.s.t.
2·317	45·1°
4·09	47·5°
9·28	54·85°
14·54	62°

C. Paraffin boiling at 124—132°. Aqueous acetic acid melting at "2·77°" and containing 10·1 per cent. of water.

Paraffin. Per cent.	c.s.t.	Paraffin. Per cent.	c.s.t.
0	23·5°	6·17	33·05°
1·054	25·2°	8·98	37·6°
1·31	25·5°	10·17	39·0°
2·08	26·8°	17·17	50·1°
3·926	29·7°		

It is to be remarked that the presence of 1 per cent. of the paraffin boiling at 124—132° produces the same rise, 1·6°, in the c.s.t. whether aqueous acetic acid melting at "0·9°" or at "2·77°" is used.

Estimation of Petroleum in Industrial Toluene.

Several specimens of industrial toluene were examined, including some which had been purified to meet the Government standard, and boiled within $0.5°$. Before determining the c.s.t., the toluene was shaken with small quantities of sulphuric acid (95 per cent.) until the acid no longer became coloured. It was then shaken with aqueous sodium hydroxide, washed with water, dried with calcium chloride, and fractionated through an eight-bulb still-head.

FIG. 6.

Critical Solution Temperatures
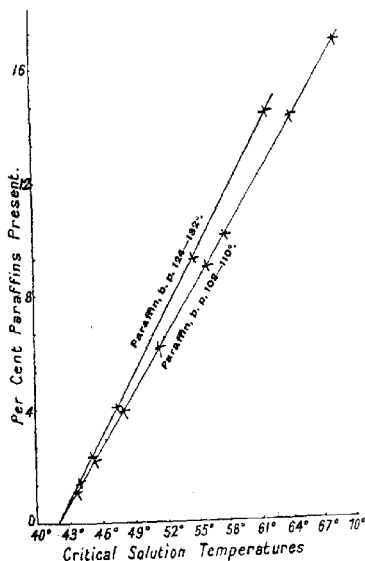
(The "Government" toluene gave a c.s.t. of $44.5°$ with "$0.9°$" acetic acid; a specimen of toluene of French official origin, a c.s.t. of $44.3°$; and a specimen of toluene supplied by English distilleries, a c.s.t. of $44.0°$.)

Three fractions were collected of the material which distilled within $0.5°$, a small first fraction, a main fraction, and a small residue. The c.s.t.'s with aqueous acetic acid (m. p. "$0.9°$") were respectively $44.35°$, $44.4°$, and, with the residue, $45.2°$, whereas pure toluene gives a value of $41.8°$.

R R

Thus but little elimination of impurity is effected by the fractionation; the c.s.t. of the 15 c.c. residue is only $0.8°$ above the main fraction, which has a value $2.6°$ above that of pure toluene. The chemical treatment and the fractionation would remove all impurity save paraffin hydrocarbons of similar boiling points, which, as is well known, are commonly found in the usual sources of toluene. The presence of xylene as the cause of the high value of the c.s.t., beyond a trace, is, apart from all else, completely excluded, inasmuch as an elevation of $2.6°$ would require from 8 to 9 per cent. of xylene (Fig. 2, Y).

If paraffin of about the boiling point 124—132° is taken as the main impurity, then, from the data given in the foregoing, the toluene contains 1.6 per cent. (by weight) of paraffins. If paraffin of about the boiling point 109—110° is the impurity, the toluene contains 1.85 per cent.

Some additional light is thrown on the problem by comparison of the densities, as the following results show. The specimen of industrial toluene, having a c.s.t. of $44.4°$, has $D_{12.4}^{12.4}$ 0.8721. Pure toluene containing 1.6 per cent. of paraffin boiling at 124—132° has the same c.s.t. and $D_{12.4}^{12.4}$ 0.8718, whilst toluene containing 1.85 per cent. of paraffin boiling at 109—110° has again the same c.s.t. but $D_{12.4}^{12.4}$ 0.8710.

It may be inferred that the toluene contains somewhat less than 1.6 per cent. of paraffins, which distil over a range probably somewhat above 124—132°.

Direct estimation of the paraffin by Spielmann and Jones's (*J. Soc. Chem. Ind.*, 1917, **36**, 490) modification of Wilson and Roberts's method does not apparently give a very accurate result with such a small proportion of paraffin.

The paraffin was isolated in a similar way from a large volume of toluene distilling within $0.5°$; it had $D_{14.4}^{14.4}$ 0.7312. The density of octane (b. p. $125.5°/760$ mm.) is given as 0.7188 at 0°, and of nonane (b. p. $149.5°/760$ mm.) as 0.733 at 0°.

We think it may be fairly claimed that the critical solution temperatures of aqueous acetic acid with industrial benzene, toluene, or xylene which have been fully purified afford an accurate means of determining the content of paraffin hydrocarbons.

We intend to pursue the study of ternary mixtures, and especially of the use of the critical solution temperatures of such mixtures as a criterion of purity of liquids.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.   [*Received, July 22nd*, 1919.]

XCII.—*Thiocyanoacetone and its Derivatives and Isomerides.*

By JOSEPH TCHERNIAC.

THIOCYANOACETONE, $SCN \cdot CH_2 \cdot CO \cdot CH_3$, was first obtained by the action of monochloroacetone on barium thiocyanate in alcoholic solution (Hellon and Tcherniac, *Ber.*, 1883, **16**, 349). Later it was found that the reaction takes place in the absence of alcohol when the crystallised barium salt is intimately mixed with mono-chloroacetone (Tcherniac, *Ber.*, 1892, **25**, 2623). Further investigation has shown that an aqueous solution of any thiocyanate of the alkalis (except that of ammonia) or of the alkaline earths can be used with advantage. As an example, the preparation by means of the sodium salt may be described.

To 92·5 grams (1 mol.) of monochloroacetone,* 191·4 c.c. (1·1 mols.) of a 46·55 per cent. solution of sodium thiocyanate were added, and the mixture was stirred for ten hours. The temperature rose about 25°, and a brown oil gradually separated. The whole product, oil and aqueous solution, was completely extracted with ether. The ethereal extract, which contained an appreciable quantity of dissolved thiocyanate, was shaken with successive quantities (10 c.c.) of water until the wash-water gave only a slight reaction with ferric chloride. The united washings, which contained some thiocyanoacetone, were reserved for addition to the following preparation before the ether extraction.

The ether was distilled off from a water-bath at the lowest temperature possible. Fifty c.c. of distilled water were added to the residue, and the whole was heated in a water-bath to 40—50° under 14 mm. pressure. The water distilled over, carrying with it some chloroacetone and its impurities, together with a very small quantity of thiocyanoacetone (0·35 gram).

The residue was dried in a vacuum over sulphuric acid, and analysis showed it to be nearly pure thiocyanoacetone (108—109 grams = 95 per cent. yield).

Purification of Thiocyanoacetone.—Thiocyanoacetone cannot be distilled without decomposition in the ordinary vacuum of the water-pump—about 14 mm. (Tcherniac, *Ber.*, 1892, **25**, 2625). It distils, however, unaltered under a pressure of about 1 mm. A portion of the thiocyanoacetone prepared as above was placed in an Anschütz distillation flask with collar and sealed-on receiver.

* Prepared by Fritsch's method (*Ber.*, 1893, **26**, 597), using magnesia instead of marble, and carefully fractionated. It contained traces only of chloroacetone.

Ground in the neck of the receiver were a U-tube filled with calcium chloride and potassium hydroxide, and a Hittorf tube. The apparatus was exhausted by means of a mercury pump, the flask being heated in a water-bath. With purple light in the Hittorf tube, most of the oil, evaporating from the surface without visible boiling, passed over at 73·5—74·5°, and was collected separately. The distillate was a highly refracting, colourless oil having D_{15}^{15} 1·1892. Analysis gave results showing close agreement with the formula C_4H_5ONS.

On keeping, especially in the light, the oil gradually became yellow, and finally dark-coloured.

Action of Hydrochloric Acid on Thiocyanoacetone.

It has already been shown that dilute aqueous hydrochloric acid does not produce any great alteration in thiocyanoacetone (Tcherniac, *Ber.*, 1892, **25**, 2618).

When 5 per cent. of its weight of hydrogen chloride is led into thiocyanoacetone, kept cool, a crystalline magma is formed which liquefies on keeping. On extraction with ether, the thiocyanoacetone is recovered apparently unaltered. A quite different result is obtained when the substance is saturated with hydrogen chloride.

Thiocyanoacetone (115 grams:1 mol.) was saturated with hydrogen chloride (70 grams), the whole being cooled with running water. After the resulting magma had completely liquefied, the syrup was dissolved in 500 c.c. of water, and the solution extracted with ether. The latter left on distillation 70 grams of a pale brown oil, which was distilled under 14 mm. pressure from a water-bath, and gave 40 grams of a colourless distillate passing over at 69°.

In another preparation the solution was distilled in a current of steam instead of being extracted with ether, and gave half the weight of the thiocyanoacetone taken.

The oil was washed with dilute sodium hydroxide solution, dried over calcium chloride, and distilled. By far the greater part passed over at 167—167·5°/754·4 mm.

Found: C = 35·99; H = 3·2; N = 10·22; Cl = 26·43. S = 24·38.
C_4H_4NClS requires C = 35·95; H = 2·99; N = 10·48; Cl = 26·59;
S = 23·97 per cent.

Apparently this substance is 2-chloro-4-methylthiazole (I),

(I.)   (II.)
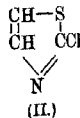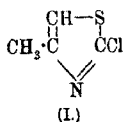
homologue of 2-chlorothiazole (II) (Schatzmann, *Annalen*, 1891, **261**, 10), the boiling point of which is 144—144·5°.

2-Chloro-4-methylthiazole is a colourless oil boiling at 167—167·5°/754·4 mm. and 69°/14 mm.; it has D$_{15}^{15}$ 1·2992. It possesses a characteristic odour resembling that of pyridine, and slightly alkaline properties; thus, it dissolves in concentrated hydrochloric acid, but not in the dilute acid. It is comparatively stable; after boiling for twelve hours with a methyl-alcoholic solution of sodium methoxide, only one-twentieth of its chlorine was removed, and the bulk of the oil remained unaltered. In this respect it differs from chlorothiazole, which is said to retain the chlorine very loosely. This is not an isolated fact. The chemical behaviour of the members of the thiazole group is often so radically different from that of their methylated homologues (see Schatzmann, *loc. cit.*) that serious doubts must arise as to their analogy of structure.

It was found that of the 70 grams of hydrogen chloride absorbed by the thiocyanoacetone, 14 grams had been consumed in the reaction

$$C_4H_5ONS + HCl = C_4H_4NClS + H_2O.$$
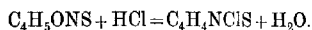
The residue from the distillation of the ethereal extract, together with the aqueous solution from which the oil had been extracted, after neutralisation with sodium carbonate and further extraction with ether, yielded 25 grams of "hydroxymethylthiazole" (after purification by crystallisation).

The action of alcoholic hydrogen chloride on thiocyanoacetone will be described later.

Thiocyanoacetone and Ammonia.

The so-called hydroxymethylthiazole, which was obtained accidentally by Hantzsch and Weber (*Ber.*, 1887, **20**, 3127) in an attempt to prepare thiocyanoacetone, owed its formation to the circumstance that they had used sodium carbonate for salting out the thiocyanoacetone. As has been shown (*Ber.*, 1892, **25**, 2619), all alkaline substances possess the power of converting thiocyanoacetone into its isomeride. Aqueous ammonia produces exactly the same result. Hantzsch's statement (*Annalen*, 1888, **249**, 7) that the chief product of the action of ammonia on thiocyanoacetone is aminomethylthiazole (thiocyanopropimine) is devoid of all foundation, as may be seen from the following experiments.

Thiocyanoacetone (115 grams : 1 mol.) was dissolved in 1500 grams of water, the solution cooled, and 50 c.c. of 20 per cent.

ammonia were added.   Heat was evolved, and a yellow resin separated.   After forty hours, the solution was filtered, and to the filtrate 172 c.c. of 25 per cent. hydrochloric acid were added, much carbon dioxide being evolved.

The acid solution was extracted with ether in the author's automatic apparatus (this vol., p. 1090), and the ethereal extract evaporated in the water-bath.   The brown, syrupy residue was heated in a vacuum on the water-bath, when some water possessing the pungent odour of thiocyanic acid distilled over.   The distillate gave the thiocyanate reaction and gradually deposited a small quantity of radially grouped yellow needles, which became dark at about 150° and decomposed at about 200° (perthiocyanogen?).

The residue from the distillation (63·5 grams) was boiled for some time with ether under a reflux condenser.   After repeated crystallisations, about 25 grams of pure "hydroxymethylthiazole" were obtained from the solution, together with a small quantity of the yellow substance above-mentioned.

If any aminomethylthiazole had been formed, it must have remained in the hydrochloric acid solution which had been extracted with ether.   This solution was therefore rendered alkaline with sodium hydroxide and completely extracted in the apparatus. The ethereal extract left on distillation 1·732 grams of a dark syrup only partly soluble in hydrochloric acid.   The hydrochloric acid solution was filtered, warmed with animal charcoal to 50°, and again filtered.   After several days, a black mud was deposited, which was filtered off.   The filtrate was warmed with charcoal (0·5 gram) and again filtered.   To the filtrate, hydrochloric acid was added, together with platinic chloride in excess, and the whole left to remain overnight, when the yellow precipitate was collected. When dry, it weighed 1·040 grams, proved insoluble in water or alcohol, and melted at about 220°.   (Found : Pt = 30·36. $(C_4H_6N_2S,HCl)_2PtCl_4$ requires Pt = 30·34 per cent.)

Assuming this to be pure double salt, it corresponds with 0·477 gram of aminomethylthiazole from 115 grams of thiocyanoacetone. Moreover, as thiocyanate is formed in the reaction, there is no reason to think that even this minute quantity of the base owes its origin to anything more than the well-known action of ammonium thiocyanate on thiocyanoacetone (Norton and Tcherniac, *Ber.*, 1883, **16**, 345).

In view of the foregoing results, Hantzsch's explanation (*loc. cit.*, p. 26; compare Beilstein, "Handbuch der organischen Chemie," IV, 518) of the formation of aminomethylthiazole (thiocyanopropimine), namely, that by the action of ammonium thiocyanate on chloroacetone, thiocyanoacetone is first formed, and is

then converted by combination with free (!) ammonia into amino-methylthiazole, must be regarded as invalid.

The Isomerides of Thiocyanoacetone : Hydroxymethylthiazole, or a-Methylrhodim.

For reasons to be stated later, the so-called hydroxymethyl-thiazole will henceforth be known as a-methylrhodim.

The author has shown (*Ber.*, 1892, **25**, 3648) how a-methylrhodim is best prepared from thiocyanoacetone. The same method may be used for its preparation direct from chloroacetone.

To 92·5 grams of monochloroacetone, 1500 grams of water, 125 grams of potassium thiocyanate (or the equivalent amount of the sodium salt), and 30 grams of sodium hydrogen carbonate are added. The mixture is shaken from time to time and allowed to remain for ten days. A brown resin is gradually deposited, and the aqueous solution is filtered off and warmed to 45°. Twenty grams of animal charcoal are then added, and the mixture is left to remain for two hours and shaken from time to time. It is then filtered, and the filtrate extracted with ether in the apparatus. On an average, there accumulated in the flask containing the ether 33 grams of white needles, which, after being washed with ether, melted at 102—103°. From the ethereal solution, a further 14 grams were obtained, making in all 47 grams, that is, approximately 41 per cent. of the theoretical yield.

Instead of extracting with ether, a tedious operation in the absence of an automatically working apparatus, the aqueous solution can be evaporated in a vacuum from a water-bath, care being taken to keep the temperature of the bath below 60° until there remain about five parts of water for one of a-methylrhodim. On cooling, 75—80 per cent. of the substance will crystallise out, and the mother liquor may be further concentrated.

When less water or sodium hydrogen carbonate is used in the preparation, the yield is smaller.

Impure a-methylrhodim is best purified by recrystallisation from five times its weight of water at 55—60°. Thus, 41 grams of the crude product were dissolved in 205 grams of water, the solution being shaken with charcoal and filtered warm. The first crop yielded 32 grams of needles melting at 102—103°.

By utilising the mode of formation from ammonium thio-carbamate (observed by Marchesini, *Gazzetta*, 1893, **23**, ii, 442), the preparation of a-methylrhodim can be much more satisfactorily accomplished than by the above method. The way there followed, namely, heating in an alcoholic solution, is unsuitable as a method

of preparation. It required thorough modification to obtain from it a simple and practical method.

Ammonium thiocarbamate, $NH_2 \cdot CO \cdot S \cdot NH_4$, is easily obtained pure by leading carbonyl sulphide into alcoholic ammonia cooled with ice. The gas is readily absorbed, and a white, crystalline powder is soon deposited, which is rapidly collected, washed with alcohol, and dried in a vacuum over sulphuric acid. Two hundred and fifty c.c. of 4·14 per cent. alcoholic ammonia yielded 18·82 grams of the dry salt.

The thiocarbamate (14·3 grams : about 0·15 mol.) was dissolved in a little water, ice added, and 12 c.c. of monochloroacetone (13·95 grams = 0·15 mol.) were mixed with the solution, and the flask was imbedded in ice. Soon a violent reaction took place, when the chloroacetone dissolved, the ice melting within the flask. The slightly yellow liquid was filtered, and the filtrate (74 grams) left to remain overnight. It set to a paste of yellowish needles (12·85 grams, dry) melting at 101—102°. From the filtrate 3·2 grams were obtained, the total of more than 16 grams representing a yield of 93 per cent. The product was easily purified by one crystallisation from water.

This result, compared with the complications attending the preparation from thiocyanoacetone, renders highly improbable the intermediate phase

$$CH_3 \cdot CO \cdot CH_2 \cdot SCN + H_2O = CH_3 \cdot CO \cdot CH_2 \cdot S \cdot CO \cdot NH_2,$$
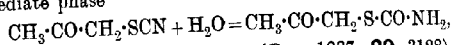
suggested by Hantzsch and Weber (*Ber.*, 1887, **20**, 3128) as part of the mechanism of the isomerisation.

a-Methylrhodim and Methyl Sulphate : Dimethylrhodim.

a-Methylrhodim (115 grams : 1 mol.) was dissolved in 500 c.c. of 2N-sodium hydroxide, and 95 c.c. of methyl sulphate (1 mol.) were gradually added, cooling with water. The solution was extracted with ether in the apparatus. The ether left 122·6 grams of a yellow oil, which solidified on cooling. When dissolved in its own volume of water, it showed a lower critical solution temperature. The slightest warmth, even that of the hand, induced separation into two layers, which mixed again on cooling. The solution was shaken with 10 grams of charcoal, filtered, the turbid filtrate concentrated in a vacuum at 35°, when it became clear again, and the concentration continued until the solution in the distillation flask weighed 145 grams. (A small quantity of oil distilled over with the water.) To the cold solution a tiny crystal from a previous preparation was added, and the whole left over sulphuric acid in a vacuum. Large crystals were gradually formed and removed

from time to time. In all, 65 grams were collected and recrystallised from a small quantity of water.

In another preparation, the crude product remaining after the distillation of the ether was drained on the vacuum pump from the oil which it contained, and was then washed with ether.

A quantity of crude product (20 grams) which had been kept for two years and had become brown and viscid was purified in the following manner. It was dissolved in water with the addition of 20 c.c. of N-sodium hydroxide and extracted with ether. The extract was almost colourless, and the aqueous solution yellowish-brown. The ether was evaporated, and left 17·322 grams of oil which soon solidified, the temperature rising to 46°. The substance was dissolved in its own weight of water at 25°, and when the solution assumed the ordinary temperature (17°), a fragment of a crystal was added. Overnight, large crystals separated (10·359 grams, m. p. 48—49°), and from the mother liquor a further crop was obtained (5·4 grams).

The original yellowish-brown solution which had been extracted with ether was acidified with hydrochloric acid and again extracted. The ether left 1·442 grams of a yellowish-brown oil which did not crystallise.

It appears from the foregoing that it will simplify the purification to add sodium hydroxide to the aqueous solution containing the product of the interaction of the sodium salt of α-methylrhodim and methyl sulphate before extracting with ether.

The substance after repeated crystallisations reached a maximum melting point, and was then analysed.

Found: C=46·22; H=5·81; N=10·52; S=25·20.
C_5H_7ONS requires C=46·51; H=5·43; N=10·85; S=24·80 per cent.

The substance is therefore dimethylrhodim,
$$CH_3 \cdot C_4H_4ONS.$$
It is very readily soluble in water or ether, and crystallises from the former in large, transparent prisms or plates melting at 49—50°.

The strong tendency of this substance to form large, well-defined crystals created a desire for the determination of its crystallographic characteristics.

This work has been kindly undertaken for me by Mr. G. M. Bennett, to whom I tender my warmest thanks. His report is as follows:

"Crystallographic examination of dimethylrhodim. Crystal system: monoclinic; holohedral class. Habit:
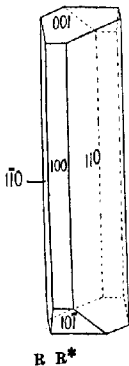
prismatic, with elongation parallel to the c-axis. Axial angle $= 98°11'$. Axial ratios : $a:b:c = 2.580:1:1.874$. Forms observed : (100), (110), (001), (10$\bar{1}$). There is a well-marked cleavage in the plane (100). "The following are the regular measurements:

	Observed.	Calculated.
100–110	68°37′	—
110–$\bar{1}$10	42 51	42°46′
100–001	81 49	—
001–$\bar{1}$01	38 40	38 43
100–10$\bar{1}$	59 28	—
001–110	86 58	87 1
$\bar{1}$01–$\bar{1}$10	79 11	79 20

"The faces of the crystals were rather dull through abrasion, particularly the small ones, so that some of the values are a little uncertain."

Hydrolysis of Dimethylrhodim.

The substance (2·58 grams) was heated with 10 c.c. of hydrochloric acid (D 1·19) for two hours at 140° in a sealed tube. There was considerable pressure on opening the tube, and the escaping gas had an odour of hydrogen sulphide and mercaptan. The contents of the tube were washed out with water and distilled, when some oil, apparently chloromethylthiazole, passed over with the water. The residual liquid was rendered alkaline and distilled into hydrochloric acid so long as the evolved vapours gave an alkaline reaction.

Part of the hydrochloride was obtained as such. After crystallisation, it gave Cl $= 52·26$, whilst $CH_3 \cdot NH_2, HCl$ requires Cl $= 52·29$ per cent. The remainder was converted into the platinichloride, which contained Pt $= 41·12$, whilst $(CH_3 \cdot NH_2, HCl)_2 PtCl_4$ requires Pt $= 41·32$ per cent.

No other base than methylamine was observed, and the total amount represented more than 90 per cent. of the theoretical.

It appears, therefore, that the methyl group introduced into the molecule of a-methylrhodim is attached to the nitrogen atom.

An attempt to prepare an O-ether from a-methylrhodim by the action of methyl iodide on the silver salt was unsuccessful. The alkaline solution is, indeed, precipitated by silver nitrate, but the precipitate consists chiefly of silver sulphide, part of the substance being destroyed.

a-Methylrhodim and Phosphorus Pentachloride.

a-Methylrhodim, which can be crystallised from warm phosphoryl chloride without any alteration, was dissolved in that solvent, a little more than the equivalent quantity (1 mol.) of phosphorus

pentachloride added, and the mixture heated to 50°. Hydrogen chloride was evolved, and a product was formed which was purified by repeated crystallisation from benzene.

Found: $S = 21\cdot74$.

C_4H_4ONClS requires $S = 21\cdot40$ per cent.

The chloride consists of pale brown, radially grouped acicular crystals melting and decomposing at 144°. It dissolves in dilute sodium hydroxide solution with a slight evolution of heat and the loss of the whole of its chlorine. On saturating the alkaline solution with carbon dioxide, a fine mud is deposited, which shrinks on drying to brown, brittle nodules (about 70 per cent. of the weight of the chloride) not melting at 220°.

The constitution of this product will be considered later.

Thiocyanoacetone and Alcoholic Hydrogen Chloride: β-Methylrhodim.

Hydrogen chloride (75 grams) was led into a mixture of thiocyanoacetone (115 grams : 1 mol.), alcohol (115 grams), and water (18 grams). On the following day, the mixture was placed in a vacuum over sulphuric acid and sodium hydroxide, and allowed to remain for several days. The brown residue (162 grams), containing a few crystals, was removed with water and extracted in the automatic apparatus. After some time, crystals began to appear both in the flask of boiling ether and in that of the aqueous solution. The extraction was continued for eight days until the crystals in the latter had disappeared. By that time, an abundance of crystals had accumulated in the ether flask, along with some brown oil. The latter was decanted with the ether, and the crystals were washed with ether and alcohol. The crystals (38 grams, dry) were dissolved under a reflux condenser in 760 grams of boiling water, charcoal was added, and the solution filtered hot. On cooling, white crystals were gradually deposited (33 grams).*

The same substance was formed when α-methylrhodim was left to remain for a long time in contact with concentrated hydrochloric acid, preferably in the presence of alcohol. A mixture of 11·5 grams of α-methylrhodim, 50 grams of hydrochloric acid (D 1·19), and 25 c.c. of alcohol yielded more than 3 grams of the substance.

Found: $C = 41\cdot41$; $H = 4\cdot54$; $N = 11\cdot93$; $S = 28\cdot11$.

C_4H_5ONS requires $C = 41\cdot74$; $H = 4\cdot35$; $N = 12\cdot17$; $S = 27\cdot83$ per cent.

---

* From the mother liquors chloromethylthiazole (18 grams) and α-methylrhodim (25 grams after purification) were obtained.

The substance, another isomeride of thiocyanoacetone, is named β-methylrhodim.

β-Methylrhodim is deposited from hot water as a white, crystalline powder; from alcohol by slow crystallisation in stout, colourless, quadratic plates melting at 183—184°. It dissolves in about 20 parts of boiling water and in about 475 parts at 15°. It is fairly readily soluble in boiling alcohol, less so in cold, and sparingly so in ether. When submitted to prolonged extraction in the apparatus with a relatively small quantity of ether, it accumulates in the boiling solvent and separates gradually in fine, colourless, transparent plates.

It is readily soluble in alkalis, and is precipitated therefrom by acetic acid.

β-Methylrhodim and Hydrochloric Acid.

β-Methylrhodim (3·45 grams) was heated with 30 c.c. of hydrochloric acid (D 1·19) for two hours at 100° in a sealed tube. There was no pressure on opening the tube, and the yellow solution yielded 3 grams of α-methylrhodim, together with a minute quantity (0·045 gram) of white crystals, which separated from the ethereal extract. They shrank, became brown at 250°, and did not melt at 265°. Whilst, therefore, β-methylrhodim is formed from α-rhodim under the influence of cold hydrochloric acid, the inverse conversion takes place almost completely at a higher temperature.

Thiocyanoacetone and Sodium Hydrogen Sulphite: iso*Methylrhodim.*

After prolonged heating of thiocyanoacetone on the water-bath, it was found to contain a crystalline substance, different from the then known derivatives. The same substance was obtained by the action of alkali hydrogen sulphites on thiocyanoacetone, and, after many attempts, a method was perfected which allowed it to be prepared with certainty and in a state of purity.

The action of free sulphur dioxide may be described first.

A solution of thiocyanoacetone (11·5 grams) in 150 grams of water absorbed 37 grams of sulphur dioxide, of which 26 grams were lost when the solution was left in a vacuum at the ordinary temperature. The solution was then extracted with ether, and yielded only 0·45 gram of a yellow oil. The extracted solution was concentrated to 20 c.c. in a vacuum on a water-bath at 40°. The residue, which still had the odour of sulphur dioxide, was again treated with ether, and yielded 8·24 grams of fairly pure thiocyanoacetone.

It would appear, therefore, that a sulphonic acid possessing a certain degree of stability is formed.

Quite different is the behaviour of thiocyanoacetone towards alkali hydrogen sulphites when they contain no free sulphur dioxide.

Thiocyanoacetone (230 grams:2 mols.) was added to a mixture of 2150 c.c. of water and 360 c.c. of a 27.8 per cent. solution of sodium hydrogen sulphite, which was neutral towards methyl-orange. The temperature rose 11°. The solution was shaken with charcoal and filtered rapidly through a folded filter. After two days there was an abundant crystallisation. The crystals were collected (72 grams, dry) and recrystallised (66.5 grams, dry) from 1450 grams of boiling alcohol.

Found: C=41.70; H=4.29; N=12.05; S=27.66.

C_4H_5ONS requires C=41.74; H=4.35; N=12.17; S=27.83 per cent.

The substance has therefore the composition of thiocyanoacetone, and is a third isomeride of that compound; it will be named *iso*methylrhodim.

iso*Methylrhodim* is remarkable for its great power of crystallisation and sparing solubility in cold water or alcohol. It requires 16 parts of boiling and 400 parts of cold alcohol. It crystallises from alcohol in white, long, brilliant, interwoven needles melting at 127—128°.

It dissolves slowly in dilute sodium hydroxide solution, but with decomposition. When the orange-coloured solution is treated with carbon dioxide, it evolves hydrogen sulphide and deposits after a time a sparingly soluble salt (sodium cyanurate?).

The sodium hydrogen sulphite used for the preparation of *iso*methylrhodim does not act solely as a catalyst. Part of the aqueous mother liquor from which the *iso*methylrhodim had been separated, and containing a trace only of sulphuric acid, was distilled with hydrochloric acid, and the distillate collected in a receiver containing water and sodium hydrogen carbonate. A portion of the distillate was oxidised with bromine, and the sulphuric acid produced was estimated gravimetrically. The result revealed the consumption of 56.13 grams of sodium hydrogen sulphite, a little more than one molecule for four molecules of thiocyano-acetone.

Preparation of iso*Methylrhodim from Chloroacetone.*

Monochloroacetone (92.5 grams:1 mol.) was stirred for two and a-half hours with 190 c.c. of a 47 per cent. solution of sodium

thiocyanate, cooling with water, when sodium chloride began to be deposited. A solution of 60 grams of crystallised potassium hydrogen sulphite in 300 c.c. of water was added, when nearly all dissolved, and the stirring was continued for half an hour. After two days, the yellow needles (44·27 grams, dry, m. p. 124—125°), containing some oil, were separated and recrystallised twice from 700 and 500 grams, respectively, of boiling alcohol, yielding, finally, 34·285 grams of white needles melting at 127—128°.

When sodium hydrogen sulphite solution was used instead of the crystallised potassium salt, the yield was much lower.

The various quantities of oil obtained in the different preparations were found to consist chiefly of thiocyanoacetone.

*iso*Methylrhodim *and Hydrochloric Acid : Dithiazylamine.*

Concentrated hydrochloric acid acts slowly on *iso*methylrhodim at the ordinary temperature, but rapidly on heating. *iso*Methylrhodim (23 grams) was boiled with 200 c.c. of concentrated hydrochloric acid and 66 c.c. of water under reflux for twenty minutes, when some hydrogen chloride was evolved. About half the liquid was then distilled off, a yellow oil passing over with the distillate. From the latter, ether extracted 1·5 grams of oil.

To the orange residue in the distillation flask, 300 grams of water were added, the whole was boiled for some time, filtered from a yellow resin, the solution treated with charcoal, and filtered hot. On cooling, faint yellow, efflorescent needles were deposited (10·2 grams, anhydrous), which were dissolved in 115 c.c. of boiling 8 per cent. hydrochloric acid, the solution being shaken with charcoal and filtered hot. On cooling, long, yellow, prismatic needles separated, which were collected and washed with the same dilute acid. After being pressed between filter paper, they weighed 13·1 grams; they contained water of crystallisation, as well as some hygroscopic moisture. In a vacuum over sulphuric acid and sodium hydroxide, they effloresced to a powder and lost about 27 per cent. of their original weight. For analysis, some of the substance was recrystallised as above.

Found : $C = 39·09$; $H = 4·53$; $N = 16·69$; $Cl = 14·57$; $S = 26·09$.

$C_8H_9N_3S_2,HCl$ requires $C = 38·79$; $H = 4·04$; $N = 16·97$; $Cl = 14·34$; $S = 25·86$ per cent.

Found : $H_2O = 27·00$.

$C_8H_9N_3S_2,HCl,5H_2O$ requires $H_2O = 26·67$ per cent.

The substance is a hydrochloride, the acid of which can be estimated by titration.

The compound crystallises in pale yellow needles which easily

lose their water of crystallisation, crumbling to a fine, yellow powder which does not melt at 250°, but appears to sublime and decompose.

One part of the anhydrous salt is soluble in 46·25 parts of water at 26° and in 3—4 parts of hot water. The hydrate is fairly soluble in concentrated and sparingly so in dilute hydrochloric acid. The latter is a very convenient solvent for its purification; thus, one part of the hydrate (equal to 0·733 part of the anhydrous salt) dissolves in about 9 parts of hot 10 per cent. hydrochloric acid, whilst it requires more than 130 parts of the cold acid of the same strength. It separates from alcohol as a yellow, crystalline powder.

The Base, $C_8H_9N_3S_2$.

The aqueous solution of the hydrochloride is precipitated by alkali hydroxides, when these are not in excess, or by alkali carbonates.

The hydrochloride (57 grams) was dissolved in 2600 grams of water, the slightly turbid solution filtered, 115 c.c. of $2N$-sodium hydroxide were added to the filtrate, and the white, voluminous, caseous precipitate was collected (48 grams, dry, instead of the theoretical 48·6 grams, m. p. 148—150°).

The 48 grams were recrystallised from 340 grams of hot alcohol. On cooling, yellowish, asbestos-like needles were deposited (38·4 grams, dry, m. p. 150—151°). The mother liquor yielded a further quantity (8·8 grams).

For analysis, the substance was twice recrystallised from a mixture of benzene and light petroleum.

Found: $C = 45·37$; $H = 4·57$; $N = 19·69$, 19·74.

$C_8H_9N_3S_2$ requires $C = 45·49$; $H = 4·27$; $N = 19·90$ per cent.

The base crystallises from the above solvent in almost white, spherical clusters of needles; from alcohol, in felt-like aggregates of long, silky needles melting at 153—154°. It dissolves in about 5 parts of hot and 37 parts of cold alcohol. It is insoluble in water or alkali carbonates, but soluble in alkali hydroxides.

Determination of Molecular Weight by the Cryoscopic Method.

Weight of solute. Gram.	Weight of of solvent. Grams.	Nature of solvent.	Δ.	M.W.
0·1077	12·945	Benzene	0·13°	313·6
0·1659	,,	,,	0·20	313·8
0·1107	19·630	Nitrobenzene	0·105	351·6
0·1674	,,	,,	0·172	357·5
			Average	334·0

$C_8H_9N_3S_2$ requires M.W. $= 211$.

Determination of Molecular Weight by the Ebullioscopic Method.

0·1939 Gram of substance in alcohol. Constant for 100 c.c. =15·6.

Rise in temperature.	Grams in 100 c.c.	M.W.
0·110°	2·938	416·7 (?)
0·137	2·620	298·3
0·120	2·365	307·4
0·107	2·154	314·0
	Average	334·0

The average happens to be the same by both methods, but the individual results are too divergent to make the average appear conclusive; it corresponds approximately with 1·5 times the simple formula $C_8H_9N_3S_2$. Since this formula cannot be multiplied by 1·5, the only recourse is to double it, unless, indeed, we admit molecular aggregation in solution, a phenomenon which does not appear uncommon in the case of complicated compounds.

A determination by Zerewitinov's method (*Ber.*, 1907, **40**, 2023; 1908, **41**, 2233) of the active hydrogen in the base, in pyridine solution, cold or hot, gave respectively 1·274 and 1·476 atoms of hydrogen per molecule of the formula $C_8H_9N_3S_2$. Of course, it is not impossible that the substance undergoes a far-reaching change under the influence of magnesium methyl iodide.

As will be seen later, when the structure of the group C_4H_4NS is discussed, the base is probably *dithiazylamine*, $(C_4H_4NS)_2NH$.

Examination of the Oil.

The oil, the second product of the action of hydrochloric acid on *iso*methylrhodim, was distilled under 14 mm. pressure several times, when it passed over at 94—97° (mostly at 96—97°), each time leaving a residue and undergoing slight decomposition. It would no doubt distil unchanged under still lower pressure.

As was to be expected, the results of the analysis were only approximate.

Found: C = 49·14; H = 5·67; S = 45·24.

C_3H_4S requires C = 50·00; H = 5·55; S = 44·44 per cent.

Determination of Molecular Weight by the Cryoscopic Method.
In Glacial Acetic Acid.

Weight of solute. Gram.	Weight of solvent. Grams.	Δ.	M.W.
0·1530	20·91	0·205°	139·2
0·3792	,,	0·515	136·3
0·5322		0·720°	137·8

$C_6H_8S_2$ requires M.W. = 144.

The formula, C_3H_4S, has therefore to be doubled.   A determination by the ebullioscopic method gave the number 188.

The compound is a colourless, highly refractive oil having a characteristic odour reminiscent of turpentine. It dissolves in concentrated sulphuric acid, yielding an orange-coloured solution which is not precipitated by water.

The formation of this substance, jointly with that of the base, may be accounted for as follows:

$$6C_4H_5ONS = 2C_8H_9N_3S_3 + C_6H_8S_2 + 2CO_2 + 2H_2O.$$
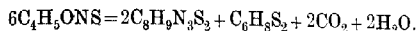
About two-thirds of the quantity of the base to be expected from this equation is obtained and one-third of the amount indicated for the compound, $C_6H_8S_2$.

The structural formula of $C_6H_8S_2$ may be represented by I, and

$$\begin{array}{cc}
CH_3\cdot\overset{}{C}\!\!:\!\!CH\cdot\overset{}{S} & \overset{5}{C}H\!\!:\!\!\overset{6}{C}H\cdot\overset{1}{S} \\
\quad\ \ \overset{}{S}\cdot CH\!\!:\!\!\overset{}{C}\cdot CH_3 & \quad\ \ \overset{}{S}\!\!-\!\!-\!\!\underset{4}{C}H\!\!:\!\!\underset{3}{C}H \\
(I.) & (II.)
\end{array}$$

if the ring (II) be termed thïen, the compound, $C_6H_8S_2$, will be
2:5-*dimethylthïen.*

*iso*M*ethylrhodim and Methyl Iodide.*

Five sealed tubes each containing 7 grams of *iso*methylrhodim, 10 grams of methyl iodide, and 20 grams of methyl alcohol were heated for three hours at 125°. On opening the tubes, the escaping gas had a fishy odour and contained carbon dioxide. The brown liquid, containing needle-shaped crystals, was removed with methyl alcohol and distilled from a water-bath. The residue (53·75 grams) was boiled with 750 c.c. of water, the solution filtered from a black tar, and boiled with charcoal. On cooling, a mixture (3·835 grams) of compact crystals (*A*) and of fine needles was deposited and separated mechanically; the latter proved to be unaltered *iso*methylrhodim.

The mother liquor was reduced by distillation to about 250 c.c. Along with the water, a small quantity of a malodorous oil and some solid matter passed over, which gave an ethereal extract of 0·622 gram.

The aqueous residue from the distillation was boiled with animal charcoal and filtered hot. On cooling, crystals (1·4 grams) similar to (*A*) were deposited.

The filtrate was now concentrated to 50 c.c., and yielded a further quantity (2·67 grams) of the same substance. The final mother liquor (*B*) will be mentioned later.

The three crystallisations of (A), together weighing about 7 grams, were dissolved in 400 grams of boiling water, the solution treated with charcoal, and filtered hot. The crystalline deposit (4·405 grams, dry) was recrystallised from 135 grams of water, and yielded 3·467 grams of long, colourless, massive crystals not melting at 265°. When heated on platinum, they sublimed without melting (Found: C = 27·80; H = 2·53; N = 33·09. CHON requires C = 27·90; H = 2·33; N = 32·72 per cent.).

The substance has therefore the composition of cyanuric acid, the properties of which it possesses. Thus, it gives Hofmann's reaction with sodium hydroxide and Wöhler's with copper sulphate.

The final mother liquor (B) was distilled in a vacuum to dryness, and the residue (23·51 grams) crystallised from alcohol. White plates (13·07 grams) were obtained which volatilised completely at about 220° with the evolution of iodine (Found: C = 18·15; H = 4·54; S = 15·47; I = 61·54, 62·13. C_3H_9SI requires C = 17·65; H = 4·41; S = 15·68; I = 62·25 per cent.).

The compound is therefore trimethylsulphine iodide.

It thus appears that under the influence of methyl iodide at a comparatively low temperature, *iso*methylrhodim undergoes complete disruption.

Comparative Examination of the Three Rhodims.

Determination of Molecular Weight by the Cryoscopic Method.

a-Methylrhodim, m. p. 103—104°.

Weight of solute. Gram.	Weight of solvent. Grams.	Nature of solvent.	Δ.	M.W.	Average.
0·1342	21·385	Nitrobenzene	0·26°	173·8	—
0·0845	,,	,,	0·14	183·8	178·8
0·3380	27·925	Glacial acetic acid	0·405	114·1	—
0·3412	,,	,,	0·40	117·1	115·6

β-Methylrhodim, m. p. 183—184°.

0·094	22·005	Glacial acetic acid	0·110°	151·4	—
0·1604	,,	,,	0·14	203·0	177·0

isoMethylrhodim, m. p. 127—128°.

0·1080	19·57	Nitrobenzene	0·105°	378·0	—
0·079	,,	,,	0·065	404·7	391·35

Determination of Molecular Weight by the Ebullioscopic Method.

In alcohol: constant for 100 c.c., 15·6.

Preliminary tests with acetanilide gave an average M.W. = 157 instead of 135.

a-Methylrhodim, m. p. 103—104° : 0·3312 gram.

Rise in temperature.	Grams in 100 c.c.	M.W.	Average.
0·620°	5·018	126·2	—
0·554	4·476	126·0	—
0·496	4·039	127·0	—
0·440	3·680	130·5	127·4

β-Methylrhodim, m. p. 183—184° : 0·2175 gram.

0·155°	3·295	331·6	—
0·137	2·939	334·7	—
0·125	2·652	331·0	—
0·110	2·417	342·7	336·66

iso*Methylrhodim*, m. p. 127—128° : 0·1732 gram.

0·078°	2·624	524·8	—
0·070	2·340	522·0	—
0·060	2·112	549·1	—
0·052	1·924	577·2	543·1

C_4H_5ONS requires M.W. = 115.

Owing evidently to anomalies of aggregation, the results are not so conclusive as might be desired. *a*-Methylrhodim has certainly the simple molecule C_4H_5ONS, whereas there is some uncertainty concerning the two other isomerides. The author is inclined to regard *β*-methylrhodim as $2(C_4H_5ONS)$ and *iso*methylrhodim as $4(C_4H_5ONS)$, the structure of the ring, C_4H_5ONS, not being necessarily the same in the three isomerides.

Constitution of the Three Methylrhodims.

The so-called *meso*-hydroxymethylthiazole has, according to Hantzsch and Weber (*Ber.*, 1887, **20**, 3127), the structural formula I, which is that of a tertiary alcohol or phenol. The only fact
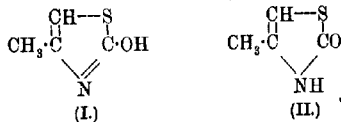
adduced by Hantzsch and Weber in favour of this formula was the alleged formation of *meso*-aminothiazoles by the action of ammonia

or primary bases. Later, however, Hantzsch had to admit the complete indifference of that compound towards ammonia or organic bases, having discovered that the reacting substance was thiocyano-acetone alone. This, and similar facts which were gradually evolved in the study of the aminothiazoles, led to these substances being represented as perfect models of tautomerism, hydroxy-methylthiazole being endowed with a ketonic double (II), in spite of the absence of properties commonly possessed by ketones, as had been pointed out by Hantzsch and Weber themselves.

The author's long acquaintance with hydroxymethylthiazole has failed to reveal to him a single fact pointing to the presence of either a hydroxyl or a carbonyl group in that compound. It behaves neither as an alcohol nor as a ketone, and it affords no justification whatever for the assumption of tautomerism, that last resort of a formula in difficulties. Furthermore, the action of phosphorus pentachloride, which, as has been shown, leaves the oxygen intact, whilst it introduces chlorine into the molecule, makes the presence of either a hydroxyl or a carbonyl group at least improbable. The two formulæ (I and II) are, however, not only improbable, but impossible, as is proved by the study of the hydrolysis of the methylated derivative, $CH_3 \cdot C_4H_4ONS$, which the author has succeeded in obtaining in a state of purity. Indeed, this substance would have to be represented as

$$
\begin{array}{c}
\text{CH---S} \\
\text{|| |} \\
CH_3 \cdot C \qquad C \cdot O \cdot CH_3 \\
\diagdown\!\diagup \\
N
\end{array}
\qquad \text{or} \qquad
\begin{array}{c}
\text{CH---S} \\
\text{|| |} \\
CH_3 \cdot C \qquad CO \\
\diagdown\!\diagup \\
N \cdot CH_3
\end{array}
$$
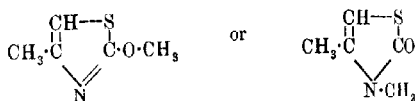
The first of these formulæ is that of an *O*-ether which can give no methylamine on hydrolysis; neither can a substance possessing the second formula, since the $N \cdot CH_3$ group is in the position 3, which, as Traumann (*Annalen*, 1888, **249**, 44) has shown in the case of 2-imino-3:4-dimethyl-2:3-dihydrothiazole (III), yields ammonia on hydrolysis, but no methylamine.

$$
\begin{array}{c}
\text{CH---S} \\
\text{|| |} \\
CH_3 \cdot C \qquad C : NH \\
\diagdown\!\diagup \\
N \cdot CH_3 \\
\text{(III.)}
\end{array}
\qquad\qquad
\begin{array}{c}
\text{CH---S} \\
\text{|| |} \\
CH_3 \cdot C \qquad C : NH \\
\diagdown\!\diagup \\
O \\
\text{(IV.)}
\end{array}
$$

The compound, $CH_3 \cdot C_4H_4ONS$, on the contrary, gives a quanti-tative yield of methylamine.

We are thus led to the conclusion that the group $N \cdot CH_3$ occupies the position 2, which brings us to the formula IV for "hydroxy-

methylthiazole." A compound of this structure may be derived from thiocyanoacetone if it is assumed that the latter passes into the enolic form, that a hydrogen atom then migrates, and, finally, that the chain is closed,

$$
\begin{array}{ccc}
\underset{\underset{O}{\big\Vert}}{\overset{\displaystyle CH_2\!\!-\!\!S}{\underset{\displaystyle CH_3\!\cdot\!C}{\big\vert}}} \;\;\; C\!:\!N
& \rightarrow &
\overset{\displaystyle CH\!\!-\!\!S}{\underset{\displaystyle CH_3\!\cdot\!C \;\;\; C\!:\!N}{\underset{OH}{\diagdown}}}
& \rightarrow &
\overset{\displaystyle CH\!\!-\!\!S}{\underset{\displaystyle CH_3\!\cdot\!C \;\;\; C\!:\!NH}{\underset{O}{\diagdown\diagup}}}
\end{array}
$$
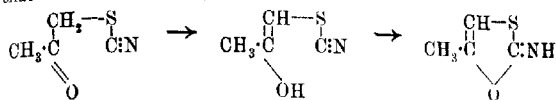
It appears, therefore, that the substance which has been known since 1887 as hydroxymethylthiazole is not a thiazole at all. It might be called 2-imino-4-methylthioxole, but for the sake of simplicity, and in view of the now proved existence of two other isomerides of thiocyanoacetone, it seems preferable to adopt the generic name *rhodim* for this class of compounds.

Thus, hydroxymethylthiazole becomes a-methylrhodim; the isomeride melting at 183—184°, β-methylrhodim; the isomeride melting at 127—128°, *iso*methylrhodim.

It has been shown that the first two can be easily converted into one another. They stand, therefore, in the closest connexion and have to be considered as structurally analogous, the only difference being in the size of the molecule, that of the β-isomeride being probably double.

The same cannot be said of *iso*methylrhodim; its chemical behaviour, which is quite different, goes to show that it possesses one of the formulæ formerly claimed by a-methylrhodim,

$$
\overset{\displaystyle CH\!\!-\!\!S}{\underset{\displaystyle CH_3\!\cdot\!C \;\;\; C\!\cdot\!OH}{\underset{N}{\diagdown\diagup}}}
\qquad \text{or} \qquad
\overset{\displaystyle CH\!\!-\!\!S}{\underset{\displaystyle CH_3\!\cdot\!C \;\;\; C\!O'}{\underset{NH}{\diagdown\diagup}}}
$$
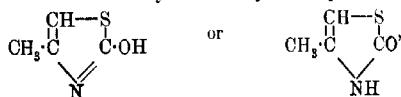
more likely the latter. A glance at it shows pre-existing the fragments, $CH_3\!\cdot\!C\!:\!CH\!\cdot\!S$, $\cdot CO\!\cdot\!NH\!\cdot$, etc., into which the compound can be made to decompose. The formula is, of course, not simple; it would have to be multiplied probably by 4, which could cause it to rank with cyanuric acid, the identity of which with tetra-carbamide has been recently demonstrated (Walters and Wise, *J. Amer. Chem. Soc.*, 1917, **39**, 2472).

The base, dithiazylamine, $C_8H_9N_3S_2$, which is formed from *iso*methylrhodim by the action of hydrochloric acid, may be represented by the formula V, which makes it appear as the parent sub-

$$
\overset{\displaystyle CH\!\!-\!\!S \quad S\!\!-\!\!CH}{\underset{\displaystyle CH_3\!\cdot\!C \;\; C\!\cdot\!N\,H\!\cdot\!C \;\; C\!\cdot\!CH_2}{\underset{N \qquad\qquad N}{\diagdown\diagup \qquad \diagdown\diagup}}}
\qquad\qquad
\overset{\displaystyle CH\!\!-\!\!S \; CH_3 \; S\!\!-\!\!CH}{\underset{\displaystyle CH_3\!\cdot\!C \;\; C\!\cdot\!N\,I\!\!-\!\!C \;\; C\!\cdot\!CH_2}{\underset{N \quad CH_3 \quad N}{\diagdown\diagup \qquad\qquad \diagdown\diagup}}}
$$

$$\text{(V.)} \qquad\qquad\qquad\qquad \text{(VI.)}$$

stance of the ammonium hydriodide, $C_{10}H_{14}N_3IS_2$, obtained by Hantzsch and Weber (*Ber.*, 1887, **20**, 3131) in small quantity by the action of methyl iodide on aminomethylthiazole, to which, starting from another direction, they assigned the structural formula VI.

The chlorinated derivative of α-methylrhodim, C_4H_4ONClS, may be

$$
\begin{array}{ccc}
\overset{\displaystyle CCl---S}{\underset{\displaystyle CH_3 \cdot C \qquad C:NH}{}} & \text{or} & \overset{\displaystyle CH---S}{\underset{\displaystyle CH_3 \cdot C \qquad C:NCl}{}} \\
\underset{\displaystyle O}{\diagdown\diagup} & & \underset{\displaystyle O}{\diagdown\diagup}
\end{array}
$$
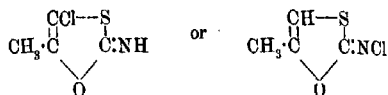
more likely the first.

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XCIII.—*An Automatic Extraction Apparatus.*

By JOSEPH TCHERNIAC.

THE extraction apparatus described by the author (*Ber.*, 1893, **25**, 3652), and frequently mentioned in the preceding paper, has undergone so many changes in the course of time that it seems desirable to give an account of it in its present shape.

The working of the apparatus is very simple. Of the two flasks shown in the diagram, the smaller one receives the ether and is heated in a water-bath; the large two-necked flask contains the solution to be extracted; it can be filled through the opening (16) of the tube (13), which is also used for siphoning off the exhausted liquor. The capacities of both flasks may vary within very wide limits, from a fraction of a litre to several litres. The two-necked flask is placed in a vessel through which cold water is run; it is then filled nearly to the neck with the liquid to be extracted, the tubes (16 and 13) are closed, and ether is poured in through the opening (17) of the tube (5). The ether flows through the tube (4) to the bottom of the flask, rises in the aqueous liquid and in the annular space between the tubes (3 and 2) (see enlarged inset), and descends through the tubes (6 and 7) into the small flask, filling the seal (9); through the condenser (10) a little mercury is poured to prevent any leakage of ether from the tap (8).

When the water-bath is heated, the vapour of ether raises the liquid ether in the seal to a certain height in the tube (6), and

also passes through the tube (2) to the bottom of the two-necked flask, where it is condensed; the liquid ether then returns through the tubes (3 and 6) and the seal into the small flask. Any aqueous
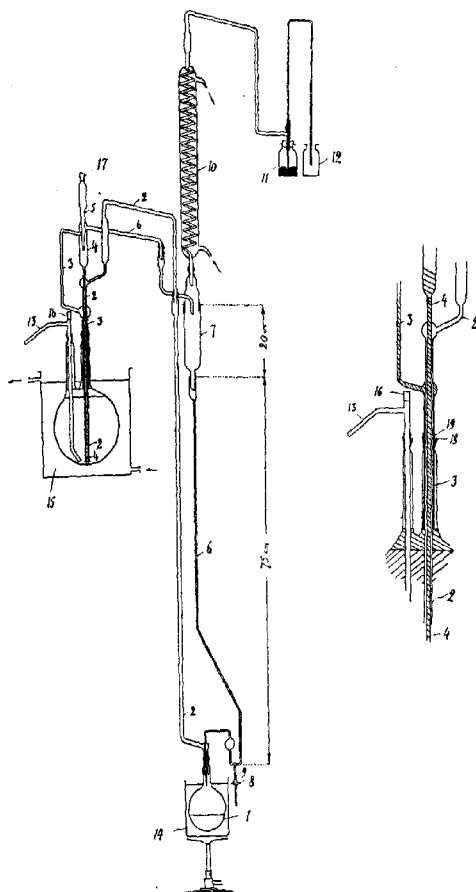
liquid carried over with the ether returns through the tube (4) into the two-necked flask.

By regulating the flow of water in the vessel (15), the tempera-

ture of the aqueous liquid can either be kept quite low or allowed to rise more or less.

The joints are very simple and efficient. As seen in the sketch (inset), the outer tube is very slightly conical (18), and the inner tube, which is little less in diameter, is provided with a short length of rubber tubing (19), which, on being pressed into the conical opening of the outer tube, makes a perfectly tight joint.

The mercury trap (11 and 12) is connected with the apparatus after the air has been expelled by the vapour of ether; it prevents losses of the solvent by diffusion.

The apparatus may be used equally well for the extraction of solid substances by means of ether, chloroform, etc. In this case, the two-necked flask may be comparatively small, and the tube (7) must be provided with a thimble or filter to arrest any particles of solid that may be carried over by the solvent. The cap of this tube is ground in.

When the apparatus is properly put together and in good order, it may be safely left to work overnight, the requisite condition for its satisfactory working being steady, uniform boiling with entire freedom from all tendency to "bumping." This is secured by the well-known device of introducing into the ether flask small tetrahedra of platinum.

Little ether is lost except that dissolved in the aqueous solution, and if care is taken before extraction to saturate the latter with sodium chloride, the loss of ether is rendered still smaller.*

In conclusion, I wish to express my thanks to my assistant, Mr. H. A. Steinmann, for the preparation of the excellent diagram of the apparatus which is the subject of this paper.

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* The apparatus can be obtained from Messrs. Baird & Tatlock (London) Ltd., 14–15, Cross Street, London, E.C. 1.

XCIV.—*The Constitution of Carbamides. Part IX. The Interaction of Nitrous Acid and Mono-substituted Ureas. The Preparation of Diazomethane, Diazoethane, Diazo-n-butane, and Diazoisopentane from the Respective Nitrosoureas.*

By Emil Alphonse Werner.

Nitrosomethylurea, obtained by von Brüning (*Ber.*, 1888, **21**, 1809), was the first example of the preparation of a nitroso-derivative from a mono-substituted urea, and its formation has been supposed to take place in accordance with the equation

$$NH_2 \cdot CO \cdot NH \cdot CH_3 + HNO_2 = NH_2 \cdot CO \cdot N(NO) \cdot CH_3 + H_2O.$$
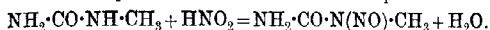
Later, nitrosophenylurea, and the corresponding *m*- and *p*-tolyl and β-naphthyl derivatives, were prepared by Walther and Wlodkowski (*J. pr. Chem.*, 1899, [ii], **59**, 285).

Assuming the carbamide configuration, it must be admitted that the formation of a nitroso-derivative is rather surprising and requires some explanation, since it would be natural to expect that the amino-group would be at once attacked with complete decomposition of the urea, thus:

(*a*) $NH_2 \cdot CO \cdot NHR + HNO_2 = N_2 + CO_2 + NH_2R + H_2O.$
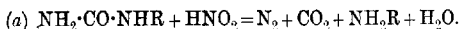
Moreover, the yield of nitroso-derivative was not sensibly affected by an addition of an excess of nitrous acid to the substituted urea, nor had nitrous acid any further action on the nitroso-compound when once formed. The latter, therefore, could not contain an amino-group.

A quantitative study of the changes involved has brought to light some interesting facts bearing on the question of the constitution of mono-substituted ureas, whilst the nitroso-derivatives examined are of more than ordinary interest, since they are likely to prove most useful substances for the simple preparation, and study, of the reactions of diazomethane and its homologues.

When methylurea in aqueous solution ($N/5$) was treated with nitrous acid in the presence of sulphuric acid, there was an immediate violent evolution of nitrogen and carbon dioxide, which ceased after a few seconds. This was quickly followed by the separation of crystals of a nitroso-derivative, the yield of which was, in round numbers, equal to 90 per cent. of the theoretical (Expts. 1 and 2).

In the case of ethyl-, *n*-butyl-, and *iso*amyl-urea, whilst similar

phenomena were observed, the yields of the respective nitroso-derivatives were approximately 76, 67, and 48 per cent. of the theoretical.

With benzylurea and phenylurea, respectively, where it was necessary to use a relatively large proportion of pure acetic acid to effect solution, 42 and 33 per cent. of the theoretical proportions of the nitroso-derivatives were formed.

The remainder of the respective ureas was decomposed according to equation (a), as proved by the evolution of larger volumes of carbon dioxide and nitrogen in proportion to the lower yields of nitroso-derivatives, and since the velocity of reaction (a) was greater than that which gave rise to the latter compounds, the evidence goes to show that the proportions of each substituted urea present in solution with a true "carbamidic" structure must be different.

In connexion with this point, it is important to note that the tendency to form a nitroso-derivative falls as the electropositive character of the hydrocarbon radicle diminishes. In the light of the facts just stated, this reaction is properly represented thus:

(b) $OH \cdot C(\colon NH) \cdot NHR + HO \cdot NO = OH \cdot C(\colon NH) \cdot N(NO)R + H_2O.$
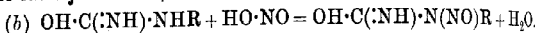
An outstanding property of the aliphatic nitroso-derivatives is their immediate decomposition by alkalis, which in the case of the methyl derivative takes place quantitatively, as follows:

(c) $OH \cdot C(\colon NH) \cdot N(NO) \cdot CH_3 + NaOH = NaOCN + CH_3N_2 + 2H_2O.$
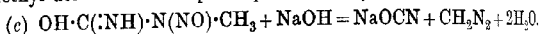
This change,* together with several other reactions described in the experimental part, supports the above constitution. It follows, therefore, that, so far as their behaviour towards nitrous acid is concerned, mono-substituted ureas in acid (sulphuric, hydrochloric, or nitric) solution are present in two forms in equilibrium, thus:

(A) $NH_2 \cdot CO \cdot NHR \rightleftharpoons OH \cdot C(\colon NH) \cdot NHR$ (B)
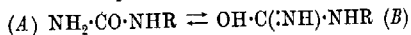
the proportion of each form being regulated by the electrochemical nature of the radicle (R).

Methylurea, for example, must be very largely presented for attack in the form (B), the formation of a salt of the type

$$OH \cdot C(\colon NH) \cdot NHR, HX$$
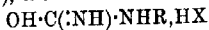
being promoted by the presence of the strongly electropositive methyl group. Phenylurea, on the other hand, is mainly present in the form (A), since the tendency to salt-formation is here distinctly feeble.

* The secondary reaction, resulting from the decomposition of diazomethane by water, is not considered here, and is dealt with later. In the case of the ethyl, n-butyl, and isoamyl compounds, some olefines are produced along with the diazo-derivative.

Further evidence in favour of the above view was found in the fact that mono-substituted ureas were directly attacked by nitrous acid in solution alone, even at a concentration of $N/18$, and whilst the velocity of the reaction at this low concentration was bound to be slow, it was quite appreciably promoted by the presence of a weak acid, such as acetic, particularly at concentration $N/5$ (Expt. 3).

In this respect, the substituted ureas differed markedly from urea itself (compare T., 1917, 111, 864), and whilst the velocity of the reaction was slow, the end result was much the same as in the presence of a strong acid.

The probable existence of a cyclic form of the urea capable of giving rise to either forms (A) or (B) by migration of hydrogen, thus:

$$
\begin{array}{ccc}
\text{NHR} & \text{H} & \\
/ & \overbrace{\quad}^{\text{NH}_2\text{R}} & \text{NHR} \\
\text{H}_2\text{N·C:O} \leftarrow & \text{HN:C} & \rightarrow \quad \text{HN:C} \\
& \text{O} & \text{OH} \\
(A.) & (C.) & (B.)
\end{array}
$$
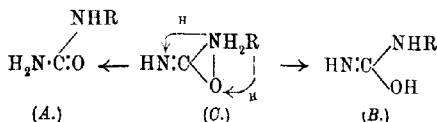
must be taken into consideration as a likely condition in a neutral solvent or in the presence of a weak acid. The diminished velocity in the reaction with nitrous acid under such conditions becomes intelligible, since form (C), like urea itself, would not be attacked by the reagent. Whilst the behaviour of di- and tri-substituted ureas towards nitrous acid is under investigation, it may be mentioned here that nitrosodiethylurea, NHEt·CO·NEt·NO, readily furnished diazoethane on treatment with either sodium hydroxide or sodium ethoxide.

EXPERIMENTAL.

Interaction of Nitrous Acid and Methylurea. Preparation and Properties of Nitrosomethylurea.

All the gasometric experiments described were performed in a Lunge nitrometer, and, for the sake of brevity, only the volumes corrected to *N.T.P.* are given in each case.

Expt. 1.—0·074 Gram of methylurea and 0·072 * gram of sodium nitrite (equal molecular proportions) were dissolved in 3 c.c. of water, and 2 c.c. of N-sulphuric acid added. The concentration was $N/5$. After one minute, there was sudden separation of crystals (the nitroso-derivative), and the evolution of gas at once ceased.

* The equivalent of 0·069 gram of *pure* sodium nitrite.

Vol. of $N_2 = 2\cdot3$ c.c. $= 10\cdot26$ per cent. of the theoretical for equation (a). Theory $= 22\cdot4$ c.c. N_2.

The gas was expelled from the nitrometer, and 2 c.c. of 15 per cent. potassium hydroxide solution were added to the residue. There was instant violent evolution of gas of a deep yellow colour (CH_2N_2), which gradually became colourless after remaining over the aqueous solution for some time.

Vol. of $N_2 = 20\cdot12$ c.c. $= 89\cdot82$ per cent. of the theoretical for the formation of the nitroso-derivative according to equation (b). Theory $= 22\cdot4$ c.c. N_2.

Expt. 2.—$0\cdot074$ Gram of methylurea and $0\cdot144$ gram of sodium nitrite were dissolved in 2 c.c. of water (HNO_2 to methylurea $= 2:1$), and 3 c.c. of N-sulphuric acid added.

Vol. of $N_2 = 2\cdot4$ c.c. $= 10\cdot71$ per cent. of the theoretical.

After addition of potassium hydroxide solution to the residue, vol. of $N_2 = 19\cdot95$ c.c. $= 89\cdot06$ per cent. of the theoretical for the nitroso-derivative, the yield of which was therefore unaffected by an excess of nitrous acid.

Expt. 3.—$0\cdot074$ Gram of methylurea and $0\cdot072$ gram of sodium nitrite were dissolved in 17 c.c. of water, and 1 c.c. of N-sulphuric acid was added. The concentration was $N/18$, and no free sulphuric acid was present. The evolution of gas was very slow, and at the end of twenty hours vol. of $N_2 = 1\cdot6$ c.c. $= 7\cdot14$ per cent. of the theoretical.

Vol. of $N_2 = 17\cdot88$ c.c. (after addition of potassium hydroxide) $= 79\cdot82$ per cent. of the nitroso-derivative formed.

Whilst the reaction in this case was not completed after twenty hours, the results prove that methylurea is directly attacked by nitrous acid alone on the same lines as in the presence of a strong acid. When an excess of acetic acid was present, the reaction was completed in about ten hours with results similar to those described in Expts. 1 and 2.

The following procedure was found most suitable for the preparation of nitrosomethylurea on a larger scale.

Methylurea ($44\cdot4$ grams) and sodium nitrite ($43\cdot2$ grams) were dissolved in 400 c.c. of water contained in a wide-mouthed bottle of 1200 c.c. capacity partly immersed in ice-cold water. A cold solution of 30 grams of pure sulphuric acid in 150 c.c. of water was gradually added, the liquid being well stirred. After two hours, the nitroso-derivative, which had separated, was collected, washed, and dried in a desiccator; it weighed $49\cdot4$ grams. The filtrate (and washings) was extracted twice with 80 c.c. of ether, from which solvent, after distillation at a gentle heat, $2\cdot2$ grams of the nitroso-compound were obtained. Total yield $= 51\cdot6$ grams, or

83·5 per cent. of the theoretical. On account of the vigorous evolution of gas and the simultaneous separation in microcrystalline form of the nitroso-compound, the latter was almost entirely carried to the surface as a thick froth; for this reason, the use of a flask should be avoided.

When sulphuric acid was replaced by about twice its equivalent of pure acetic acid in the above preparation, the nitroso-compound separated in highly refractive, tetragonal prisms, there was much less frothing, but it was necessary to allow the preparation to continue for not less than twenty-four hours before the maximum yield was attained, which even then was about 10 per cent. less than when sulphuric acid was used. Whilst individual crystals of nitrosomethylurea appear quite colourless, in bulk the compound has a pale buff colour rather than yellow, as described by von Brüning (loc. cit.). The crystals are readily soluble in alcohol, acetone, or ether, moderately so in benzene or chloroform, and almost insoluble in cold water.

On exposure to sunlight, the compound gradually loses its buff colour and becomes pale sea-green; beyond a fall in the melting point, this change had no apparent effect on the general reactions of the substance.

When an alcoholic solution of nitrosomethylurea was heated to the boiling point, it was gradually decomposed, thus:

$$OH \cdot C(:NH) \cdot N(NO) \cdot CH_3 \longrightarrow N_2 + CH_3 \cdot OH + HNCO \rightleftharpoons HOCN.$$
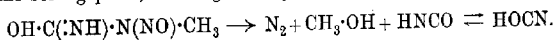
Ethyl allophanate was produced as a result of the interaction of cyanic acid and ethyl alcohol.

In connexion with this decomposition, a curious difference was found in the stability of specimens of nitrosomethylurea prepared in the presence of sulphuric acid and of acetic acid respectively.

Expt. 4.—(a) A solution of 5 grams of nitrosomethylurea (acetic acid preparation) in 70 c.c. of alcohol was boiled under reflux; the buff-yellow colour of the solution gradually disappeared, and, after two hours, the solution was colourless. On cooling, ethyl allophanate, identified by its melting point (191°) and properties, separated, and the amount ultimately obtained was 2·28 grams, or 71·24 per cent. of the theoretical (theory = 3·2 grams from 5 grams of nitrosomethylurea). (b) A similar experiment with a specimen prepared in sulphuric acid solution gave, after two hours, 27·4 per cent., and after three hours only 40·94 per cent. of the theoretical yield of ethyl allophanate. For the present, no explanation can be offered for this apparent anomaly, which has been verified with several specimens.

Nitrosomethylurea melted at 121° (crystals from ether), and in

contrast to the foregoing change was violently decomposed, as follows:

(d) $OH \cdot C(:NH) \cdot N(NO) \cdot CH_3 = N_2 + CH_3 \cdot NCO + H_2O$.

Most of the *isocyanic* ester was obtained as the polymeride, $(CH_3 \cdot NCO)_3$, which melted at 177° (Hofmann gives 176°).

Preparation of Diazomethane from Nitrosomethylurea.

In order to obtain the best yield of diazomethane in solution in ether, either of the following methods can be recommended.

Expt. 5.—Nitrosomethylurea (10·3 grams) in microcrystalline form was introduced into a round-bottomed flask of about 100 c.c. capacity, 50 c.c. of pure ether (distilled over sodium) were poured down the side of the flask, which stood in melting ice, and, without delay, 20 c.c. of 70 per cent. potassium hydroxide solution were quickly added drop by drop, while a quiet, circular motion was given to the flask. After about ten minutes, the deep golden-yellow, ethereal solution was decanted. It contained 3·2 grams of diazomethane, determined by the iodine method, which was equal to 76·2 per cent. of the theoretical for equation (c).

Whilst it was not possible to avoid decomposition of a considerable proportion of diazomethane by the water generated during the reaction, the effect was slightly reduced by altering the order of procedure; thus, when nitrosomethylurea was added in portions of about 0·5 gram at a time to very concentrated potassium hydroxide solution lying under the surface of ether, a solution of diazomethane was obtained which contained 78—79 per cent. of the theoretical.

In studying the use of diazomethane as a methylating agent, it has been apparently the universal practice to employ the substance exclusively in ethereal solution. This has obviously a serious disadvantage, on account of the limitations of ether as a solvent for many types of organic compounds. There seems no reason why this practice should be so rigidly adhered to, as shown by the following experiments.

Expt. 6.—To a solution of 1·03 grams of nitrosomethylurea in 40 c.c. of pure alcohol, a molecular proportion of sodium ethoxide in 10 c.c. of alcohol was added. Sodium cyanate was immediately precipitated, accompanied by a quiet evolution of nitrogen, which ceased at the end of about fifteen minutes, and a rich yellow solution of diazomethane was obtained. To 5 c.c. of the solution placed in the nitrometer, 10 c.c. of water were added; there was immediate brisk evolution of nitrogen, while the liquid became colourless.

Vol. of N_2 (measured over water) = 17·91 c.c. Hence for total

solution $= 179\cdot1$ c.c. Theory $= 224$ c.c. Therefore the solution contained $79\cdot9$ per cent. of the theoretical proportion of diazomethane.

Expt. 7.—A solution of $0\cdot103$ gram of nitrosomethylurea in 3 c.c. of alcohol was introduced into the nitrometer, and $0\cdot068$ gram of sodium ethoxide in 2 c.c. of alcohol was added.

After twenty hours, only $4\cdot5$ c.c. of nitrogen (corrected for pressure of alcohol vapour) were evolved.

The gas was expelled from the nitrometer, and 10 c.c. of water were added, when there was immediate rapid evolution of nitrogen. Vol. of $N_2 = 16\cdot84$ c.c. (Theory $= 22\cdot4$ c.c.)

The solution therefore contained, after remaining for twenty hours, $75\cdot3$ per cent. of the theoretical amount of diazomethane.

It will be seen from the equation,

$$OH\cdot C(:NH)\cdot N(NO)\cdot CH_3 + C_2H_5\cdot ONa = NaOCN + CH_2N_2 + H_2O + C_2H_5\cdot OH,$$
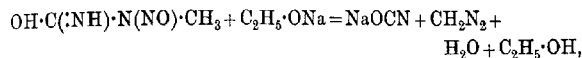
that whilst the amount of water produced was theoretically capable of decomposing all the diazomethane formed, its effect was greatly suppressed by the presence of a relatively large volume of alcohol. It may be mentioned that results very similar to those recorded in Expt. 7 were obtained when diazomethane was generated in the presence of pure methyl, propyl, *n*-butyl, and *iso*amyl alcohol respectively. Moreover, since there was no evidence of the formation of an ether ($R\cdot O\cdot CH_3$), it must be concluded that diazomethane does not attack the hydroxyl group of an alcohol.

The chief point of practical interest arising out of these observations lies in the simple application of the reaction as a method for studying the properties of diazomethane under more favourable conditions. In the case of a neutral substance, for example, it may be dissolved in alcohol,* together with a small excess of nitrosomethylurea; on addition of the requisite amount of sodium ethoxide, diazomethane is instantly generated in situ with the substance to be attacked.

Decomposition of Nitrosomethylurea by Ammonia.

When an alcoholic solution of ammonia was added to a similar solution of nitrosomethylurea cooled to $0°$, there was vigorous evolution of nitrogen, and a colourless solution was obtained. After a few minutes, a certain quantity of acicular prisms separated, which were identified as ammonium cyanate. As the

* Pure alcohol which has been finally dried by adding to it a small quantity of an ethereal solution of diazomethane may be used with advantage.

temperature was allowed to rise, the crystals redissolved.   The primary reaction was as follows:

$$OH \cdot C(:NH) \cdot N(NO) \cdot CH_3 + NH_3 = NH_4OCN \rightleftharpoons CON_2H_4 + N_2 + CH_3 \cdot OH.$$
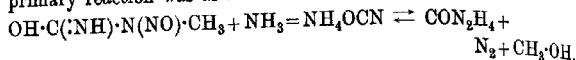
Three experiments gave yields of urea which varied from 42 to 53 per cent. of the theoretical. Methylurea and a small quantity of as-dimethylurea (which melted at 181°) were separated from the mother liquors; these were the result of (1) the methylation of ammonia, $CH_2N_2 + NH_3 = CH_3 \cdot NH_2 + N_2$, and (2) the further methylation of methylamine to dimethylamine. As the reaction progressed, each amine decomposed a portion of nitrosomethylurea according to the above equation. The further study of these reactions will form the subject of a future communication.

The Spontaneous Decomposition of Nitrosomethylurea.

It may be worth while to point out that no specimen of nitroso-methylurea could be kept unchanged for more than about five months. One preparation (about 30 grams), stocked in a dark brown, glass-stoppered bottle, decomposed spontaneously after 162 days, although only three days previously several grams removed for the preparation of diazomethane behaved in a normal manner. The decomposition was on the lines of the change produced by heat (equation d), and whilst much trimethyl isocyanurate was formed, a viscous product freely soluble in water was generated, the nature of which has not yet been elucidated.

The behaviour of a number of other substituted ureas towards nitrous acid is shown below. The experiments were carried out as described under Expt. 1.

	Vol. of N_2 evolved. C.c.	Decomposition according to equation (a). Per cent.	Yield of nitroso-derivative. Per cent.
1. Ethylurea	5·3	23·66	76·34
2. n-Butylurea.........	7·99	32·60	67·40
3. isoAmylurea	11·5	51·33	48·67
4. Benzylurea	12·97	57·90	42·10
5. Phenylurea	14·96	66·78	33·22

Nitrosoethylurea, prepared in a manner similar to the methyl derivative, was obtained in pale buff-yellow, hexagonal plates which melted at 103—104°. Diazoethane was obtained on decomposition with potassium hydroxide according to equation (c); ethylene to the extent of 14·77 per cent. of the theoretical was simultaneously formed, thus:

$$(c)\ OH \cdot C(:NH) \cdot N(NO) \cdot C_2H_5 + KOH = KOCN + C_2H_4 + N_2 + 2H_2O.$$
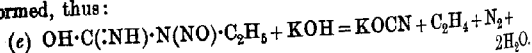
A very good yield of diazoethane in ethereal solution was readily prepared by the method described under Expt. 5.

Nitroso-n-*butylurea*,* $C_5H_{11}O_2N_3$, formed almost colourless, hexagonal plates which melted at 85°. Diazo-*n*-butane was obtained as an amber-coloured, mobile liquid with a stupefying odour by the direct addition of nitrosobutylurea to 70 per cent. potassium hydroxide solution cooled to 0°; butylene and nitrogen were simultaneously formed to the extent of about 30 per cent. of the theoretical on the lines of equation (*e*).

Nitrosoisoamylurea, $C_6H_{13}O_2N_3$, was obtained in minute, pale buff, unctuous, platy crystals which melted at 74°; since *iso*amyl-urea is sparingly soluble in water, it was necessary to use 30 per cent. acetic acid as solvent in the preparation of the nitroso-derivative.

Diazoisopentane, $C_5H_{10}N_2$, was obtained as a dark brown oil of unpleasant odour by the addition of potassium hydroxide solution to the nitrosourea.

Nitrosobenzylurea, $C_8H_9O_2N_3$, which was prepared by the action of nitrous acid on benzylurea dissolved in 50 per cent. acetic acid, formed many-sided prisms which melted at 101°; these were insoluble in water, but readily soluble in alcohol or ether.

Phenyldiazomethane, $C_6H_5 \cdot CH\colon N_2$, separated as a deep reddish-brown oil on the addition of the nitroso-compound to a 70 per cent. solution of potassium hydroxide.

Summary.

(1) The interaction of mono-substituted ureas and nitrous acid in two directions, with (*a*) production of nitroso-derivatives, and (*b*) the complete disruption of the molecule, is explained by the presence in solution of two structural forms of the urea in equilibrium.

(2) The nitroso-derivatives are shown to have the constitution $OH \cdot C(\colon NH) \cdot N(NO)R$, and their formation is promoted in proportion to the electropositive character of the radicle (R) in the original urea.

(3) The aliphatic nitroso-derivatives are decomposed by alkalis with the production of diazo-derivatives of the paraffins in very good yields.

* n-*Butylurea*, $C_5H_{12}ON_2$, from which the nitroso-derivative was obtained' has not been hitherto described. It was readily obtained by evaporating at 100° an aqueous solution of *n*-butylamine hydrochloride and potassium cyanate. It formed crystals which melted at 86° and were readily soluble in water or alcohol.

(4) It is shown that diazomethane and its homologues may be conveniently prepared in alcoholic solution for the study of their reactions.

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XCV.—*Dyes Derived from Quinolinic Acid.*

By PRAPHULLA CHANDRA GHOSH.

THE object of the present investigation was to prepare dyes from quinolinic acid analogous to the phthaleins, and to compare their colour and fluorescence. That quinolinic acid condenses with phenol and resorcinol has, indeed, been mentioned by Noelting and Collin (*Ber.*, 1884, **17**, 258), but few details were given, and the products were not analysed. A compound from quinolinic acid and hydroxyquinol has been described by Liebermann and Wölbling (*Ber.*, 1902, **35**, 1786). In the present work, the condensation of quinolinic acid with resorcinol, catechol, phloroglucinol, *m*-phenylenediamine, *m*-dimethylaminophenol, and 2:4-diaminophenol has been effected. These condensations take place without the use of any condensing agent by simply heating the two constituents together.

In comparison with the corresponding phthaleins, the effect of the presence of the nitrogen atom in the ring is to lighten the colour and to diminish the fluorescence. In this series of compounds, the greater the power of an auxochromic group to deepen the colour, the greater is its effect on fluorescence. The compound obtained from quinolinic acid and *m*-dimethylaminophenol has the deepest colour and is the most strongly fluorescent.

Dyes analogous to hydroxyanthraquinones have not yet been prepared, but work in this direction is being continued.

EXPERIMENTAL.

Quinolinic acid was prepared by oxidising a solution of quinoline (10 grams) in acetone (150 c.c.) with a 5 per cent. aqueous solution of the theoretical quantity of potassium permanganate at about 10°.

If the manganese dioxide is dried in the air, powdered, and then extracted with alcohol, the solution, on concentration, deposits pale yellow needles melting at 71—72° This substance is insoluble in

alkali hydroxides and volatile with steam. The amount obtained was sufficient only for an estimation of nitrogen:

0·1145 gave 17·6 c.c. N_2 at 31° and 756 mm. N = 17·16 per cent.
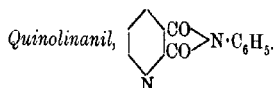
Quinolinanil,

Half a gram of quinolinic acid and 2 c.c. of aniline were heated on the sand-bath for ten to fifteen minutes, when the whole of the acid dissolved. On cooling, crystals separated, which were collected and washed with alcohol. They formed colourless, prismatic needles melting at 248—251° (Engler, *Ber.*, 1894, **27**, 1789, gives 228°) (Found: N = 13·4. $C_{13}H_8O_2N_2$ requires N = 12·50 per cent.).

Quinolinylphenylhydrazine,
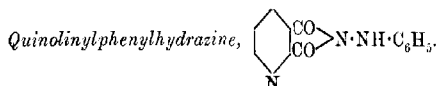
Half a gram of the acid was heated with 2 c.c. of phenylhydrazine for about ten minutes. The clear solution, on cooling, became syrupy, and on adding alcohol, crystals were obtained which, when collected and washed free from phenylhydrazine, melted and decomposed at 237—238°:

0·099 gave 15·9 c.c. N_2 at 31° and 755 mm. N = 17·68.

$C_{13}H_9O_2N_3$ requires N = 17·55 per cent.

Resorcinolquinolinein,
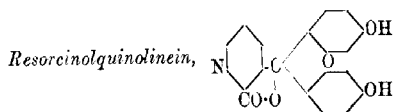
Two grams of quinolinic acid and 4 grams of resorcinol were heated at 180—200° for two hours. Some violet colouring matter sublimed, which might have been due to the formation of a substance resembling 1 : 3-dihydroxyanthraquinone. On cooling, the fusion was extracted with alcohol, and the dye was precipitated from the alcoholic extract with water. It could not be crystallised. It melts and decomposes at 266—267°. It is fluorescent in alcohol, acetone, or toluene, and aqueous potassium hydroxide gives an orange-green fluorescence:

0·1020 gave 0·2550 CO_2 and 0·032 H_2O. C = 68·1; H = 3·48.

$C_{19}H_{11}O_5N$ requires C = 68·46; H = 3·33 per cent.

The *silver* salt was prepared in the ordinary way:

0·2132 gave 0·1092 AgCl.   Ag = 38·6.

$C_{19}H_9O_5NAg_2$ requires Ag = 39·5 per cent.

Catecholquinolinein.

This compound has not yet been obtained in sufficient quantity for analysis. It is prepared and purified in the same way as the above compound.   It dissolves in aqueous potassium hydroxide with a greenish-blue colour.

Phloroglucinolquinolinein,
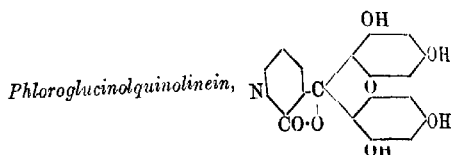
Two grams of quinolinic acid and 4 grams of phloroglucinol were heated at 130—150° for about ten minutes.   At first the mixture melted, the colour changing to red, and then the whole solidified. On crystallisation from water, a red compound melting and decomposing at 275—277° was obtained, which was very readily soluble in alcohol:

0·100 gave 0·2277 CO_2 and 0·0289 H_2O.   C = 62·1; H = 3·21.

$C_{19}H_{11}O_7N$ requires C = 62·46; H = 3·01 per cent.

If the solid mass is dissolved in alcohol and the solution concentrated, a pale yellow, crystalline compound is obtained which does not melt at 295°.   It dissolves in aqueous potassium hydroxide with a yellow colour like the hydroxybenzophenones, and is more readily soluble in water than the compound just described. It has not been obtained in sufficient quantity for analysis.

m-Phenylenediaminequinolinein,
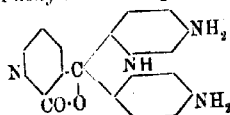
One gram of quinolinic acid and 3 grams of *m*-phenylenediamine hydrochloride were heated slowly to 210° and kept at 210—220° for twenty to twenty-five minutes.   After cooling, the mass was extracted with alcohol and filtered; the solution was fluorescent

The dye was obtained in a pure state by adding ether to the alcoholic solution.   It melts and decomposes at 232—235° :

0·103 gave 15·4 c.c. N_2 at 30° and 758 mm.   N = 16·73.

$C_{19}H_{14}O_2N_4$ requires N = 16·97 per cent.

m-*Dimethylaminophenolquinolinein*,
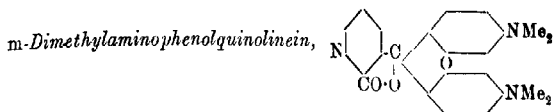
Quinolinic acid (0·75 gram) and *m*-dimethylaminophenol (1·5 grams) were heated at 120—130° for fifteen to twenty minutes, and then the temperature was slowly raised to 150°, when heating was stopped.   The mass was extracted with alcohol, and the dye precipitated from the solution with water.   When crystallised from dilute alcohol, it melted and decomposed at 148—151°.   The alcoholic solution shows a reddish-violet fluorescence, which is deeper in acetic acid or alcoholic hydrochloric acid :

0·1062 gave 10·8 c.c. N_2 at 32° and 751·4 mm.   N = 11·1.

$C_{21}H_{21}O_3N_3$ requires N = 11·5 per cent.

2 : 4-*Diaminophenolquinolinein*,
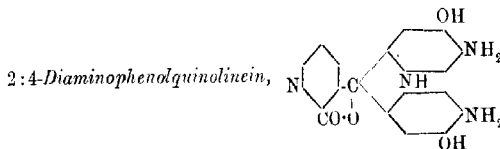
One gram of quinolinic acid and 3 grams of 2 : 4-diaminophenol hydrochloride were slowly heated to 180° and kept at this point for a few minutes.   The dye was extracted by boiling with alcohol and filtering from the unchanged diaminophenol hydrochloride.   It was purified by dissolving in alcohol and precipitating with water, but could not be crystallised.   It does not melt at 290°.   The compound is reddish-brown, and its solution in alcohol is fluorescent:

0·101 gave 13·8 c.c. N_2 at 30° and 756 mm.   N = 15·37.

$C_{19}H_{14}O_4N_4$ requires N = 15·47 per cent.

In conclusion, I beg to express my great indebtedness to Sir P. C. Rây for the loan of 200 grams of quinoline.

XCVI.—*Sodium Hypochlorite.*

By MALCOLM PERCIVAL APPLEBEY.

SODIUM HYPOCHLORITE in a solid form was first obtained by Muspratt and Shrapnell Smith, of the United Alkali Co., Ltd., in the course of investigations directed towards the preparation of very concentrated solutions (*J. Soc. Chem. Ind.*, 1898, **17**, 1096; 1899, **18**, 210; 1903, **22**, 591). Their preparations were obtained by cooling concentrated solutions, and had a composition corresponding approximately with a hexahydrate. The product melted in its water of crystallisation at 20°, and the fusion was unstable. It could be dehydrated slowly by means of a current of dry air under diminished pressure, and had then a melting point of 45°, but the results were deemed to be of no commercial value, and the investigations were accordingly discontinued.

It was suggested by Mr. Muspratt that a complete investigation of the hydration and solubility relationships might furnish information of both scientific and industrial value, and a preliminary survey of the field has accordingly been made. This has already yielded results of some importance, which are the subject of this communication. They are to be regarded as provisional, and will be followed at a later date by a systematic phase-rule treatment.

Preparation and Properties of Muspratt's Hydrate.

The hypochlorite solutions were prepared by treating 35 per cent. sodium hydroxide solution cooled in ice-water with chlorine, removing the precipitated sodium chloride, adding sodium hydroxide equivalent to the sodium chloride separated, and repeating the treatment with chlorine until the solution was about $5N$ when tested with neutral sodium arsenite solution. On a few occasions, preparations were lost owing to spontaneous transformation to chlorate and chloride. Such transformation, when it sets in, takes place with extreme rapidity in concentrated solutions, and is accompanied by the evolution of considerable quantities of gas consisting of both chlorine and oxygen. The transformation to chlorate can, however, be prevented by observing the three conditions laid down by Muspratt and Shrapnell Smith, namely, (1) low temperature; (2) absence of iron or other heavy metals which act as catalysts; (3) presence of excess of free alkali. The solution, which has been freed from precipitated sodium chloride, is

now cooled to about $-10°$ in a freezing mixture and induced to crystallise, either by shaking or by impregnating with a crystal from a previous preparation. The hypochlorite then separates as a mass of very fine, hair-like crystals filling the whole liquid, whilst the temperature rises considerably. When the whole has again reached the temperature of the freezing mixture, the crystals are separated from the mother liquor by suction through a Büchner funnel without filter paper or asbestos, the form of the crystals being such as to make their retention easy. The crystals are pressed down to remove adhering mother liquor, and then appear to be colourless at the top, although the mass in the lower part of the funnel is green, owing to the presence of mother liquor, which cannot be entirely removed, being formed anew by deliquescence during filtration. The crystals liquefy at temperatures varying between $18°$ and $19°$, according to their purity. The fusion is not quite transparent, but becomes so at a somewhat higher temperature. This behaviour, in conjunction with the subsequent separation of a lower hydrate on cooling, appears to show that the hydrate does not melt completely, but undergoes a transformation at about $19°$ to a lower hydrate, formed in very small quantity, and its saturated solution, which has almost the same composition as the original crystals.

Analysis of the crystals gave somewhat unsatisfactory results, since, owing to the low melting point and rapid deliquescence, it was difficult to secure a sample in a sufficiently dry state. After several trials, it was found best to filter off a small quantity in a Gooch crucible without asbestos, and to break up the crystals in the crucible with a spatula while the suction continued. All attempts to dry the crystals with filter paper failed, owing to the rapid oxidising action on the paper, which resulted in the development of heat, and after a time led actually to charring of the paper. For analysis, the substance was weighed out and dissolved in water, and aliquot parts of the solution were titrated against arsenite for active chlorine and against silver nitrate and thiocyanate for total chlorine after reduction of the hypochlorite with the correct amount of arsenite solution. The following analytical data refer to two specimens which gave for total chlorine quantities not greater than would be formed from the hypochlorite present, and were therefore free from chloride:

Sample I, prepared by twice recrystallising after fusion:

1·1147 gave active chlorine $0·4065 = 36·47$.
            H_2O (by difference) $0·6899 = 62·07$.

Sample II, prepared by synthesis from the pentahydrate:
$0\cdot5020$ gave active chlorine $0\cdot1807 = 35\cdot99$.

H_2O (by difference) $0\cdot3123 = 62\cdot21$.

$NaOCl,7H_2O$ requires active chlorine $= 35\cdot36$. $H_2O = 62\cdot88$ per cent.

$NaOCl,6H_2O$ requires active chlorine $= 38\cdot85$. $H_2O = 59\cdot21$ per cent.

From these data, it would appear that Muspratt's hydrate nearer in composition to a heptahydrate than to a hexahydrate At the same time, the agreement with the heptahydrate formula j by no means good, and it may be found on further investigatio that more than one hydrate is present in the crystals prepared b Muspratt's method.

Sodium Hypochlorite Pentahydrate.

When the cloudy liquid obtained by heating the heptahydrate to $20°$ is allowed to cool slowly to the ordinary temperature, largi and well-formed crystals of a new hydrate are obtained. The crystals are greenish-yellow, and contain a considerable amount of mother liquor; when they are broken up in an agate mortar, a separation of liquid takes place, and the powdered substance must be freed from this liquid by filtration through a Gooch crucible.

When prepared in this way, the substance gave the following analytical results:

	I.	II.	Calculated for $NaOCl,5H_2O$.
Weight of substance	0·3482 gram	0·3786 gram	—
Active chlorine	0·1473 ,,	0·1615 ,,	—
,, ,. per cent. ...	42·32	42·66	43·10
Cl as chloride	0·0006	nil	—
Water (by difference)	0·1929 gram	0·2090 gram	—
,, per cent.	55·40	55·20	54·75
Loss on heating	63·51	—	64·47

The pentahydrate melts at $27°$, and is thus a much more practicable substance than the heptahydrate. The fusion is in this case also somewhat cloudy, but the nature of the suspension cannot yet be definitely stated. Up to the present, a small amount of decomposition has always taken place during melting. The pentahydrate is very deliquescent, but the crystals are not unstable at the ordinary temperature if kept in a well-stoppered bottle; a specimen kept for more than a week in a corked test-tube in a well-lighted laboratory showed no measurable increase in chloride content, although some deliquescence had taken place.

The mother liquor from which the pentahydrate has separated

may be made to give a further yield of pentahydrate by freezing out heptahydrate, heating the latter to 20°, and allowing to crystallise as before. By this procedure, there is no difficulty in converting at least 50 per cent. of the heptahydrate into the corresponding amount of pentahydrate.

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XCVII.—*Capsaicin. Part I.*

By ARTHUR LAPWORTH and FRANK ALBERT ROYLE.

CAPSAICIN, the pungent principle of the fruit of various species of the genus *Capsicum*, was first isolated in crystalline form by Thresh (*Pharm. J.*, 1876, [iii], **7**, 21, 259, 473; 1877, **8**, 187) and assigned by him the formula $C_9H_{14}O_2$. Micko (*Zeitsch. Nahr. Genussm.*, 1898, 818) showed that the substance contained nitrogen, and as a result of analyses and molecular-weight determinations deduced the formula $C_{18}H_{28}O_3N$.

Thresh showed that capsaicin is a phenol, but did not discover any other very marked chemical characters; Micko, whose contributions are probably of most importance amongst those of subsequent investigators, established the fact that the molecule of capsaicin contains one phenolic hydroxyl group and one methoxyl group, and this, on the basis of his empirical formula, leads to the expression $C_{17}H_{24}ON(OH)(O \cdot CH_3)$ for the substance. Micko prepared the indifferent benzoyl derivative and observed that under certain conditions capsaicin undergoes slight decomposition, emitting a faint odour reminiscent of vanillin.

A comprehensive bibliography of the subject is given in Thorpe's "Dictionary of Applied Chemistry" (1913, **4**, 559).

The present authors began the investigation of the subject in 1914, at which time the only significant data bearing on the chemical nature and structure of capsaicin were the facts above cited. Their study was greatly retarded by other work arising out of the war, and in view of this fact, and especially as the active interest in compounds with pungent characters has been manifested in countries where scientific research has had no such serious setback as here, it is thought desirable to place on record the progress which has now been made.

The authors have examined various methods previously used for isolating pure capsaicin from the crude extract made from the seeds

and have worked out a process which combines a number of devices some of which are based on details of the processes suggested by previous workers, but as a whole appears especially simple in practice.

The properties of capsaicin which have been described by Thresh, Micko, and by Nelson (*Chem. News*, 1911, **103**, 111) have been confirmed in all essential details, but the analyses made have consistently pointed to the formula $C_{18}H_{27}O_3N$ or
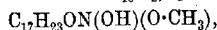
$$C_{17}H_{23}ON(OH)(O \cdot CH_3),$$

and not that proposed by Micko, which contains one more atom of hydrogen and is inconsistent with the normal valencies of these four elements in carbon compounds.

The methyl derivative, $C_{17}H_{23}ON(O \cdot CH_3)_2$, hereafter termed methylcapsaicin, has been prepared and characterised; it is non-phenolic and is much less pungent than the parent substance.

Both capsaicin and methylcapsaicin are feebly basic. They are extremely stable towards hot concentrated alkali hydroxides, but are very slowly attacked by hot acids; the products of hydrolysis have not been determined, but ammonia is always one of them, methylamine being entirely absent. The action of phosphorus pentachloride on methylcapsaicin yields a small quantity of a volatile, nitrogenous oil; this the authors suspect to be the nitrile of a fatty acid, but have not yet had the opportunity of examining it closely.

Most attention has been paid, in the first instance, to the action of reducing agents, many of which evidently attacked capsaicin to a certain extent (as was evidenced by the ready formation of ammonia or ammonium salts), without any obvious general destruction or charring.

From the more highly purified capsaicin, reduced by means of sodium and ethyl alcohol, ammonia was obtained and also, among other products, a small quantity of a compound, the bulk of which boiled at about 216—217° and had the odour and general properties of a fatty alcohol.

Oxidation of methylcapsaicin takes place readily, and among other products veratric acid, $C_6H_3(OMe)_2 \cdot CO_2H$, was the most readily recognised. There was also formed a fatty acid, of which scarcely sufficient was obtained to identify with complete certainty.

Even disregarding such of the above considerations as are yet not fully substantiated, it is probable that capsaicin is a C-disubstituted derivative of one of the isodynamic forms of dihydro-oxazole:
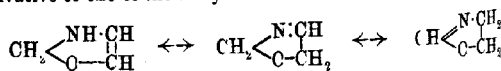
EXPERIMENTAL.

Isolation of Capsaicin.

The ordinary alcoholic extract of capsicums consists mainly of gum or dextrin-like compounds, soluble in water, together with substances which have the characters of saturated and unsaturated carboxylic acids, and relatively small amounts of fats.

In order to isolate capsaicin from this mixture advantage is taken of the fact that capsaicin does not form a stable barium salt when it is brought into contact with aqueous barium chloride which has been rendered ammoniacal. In the same circumstances, however, the free carboxylic acids present in the extract are mainly precipitated as barium salts which are for the most part insoluble in water, alcohol, or ether, or, more especially, in acetone. The gum-like substance present remains dissolved in the water, which retains only traces of capsaicin easily recovered by extraction with ether, and the bulk of the active principle, together with the fats, is found in the precipitate. On extraction of the precipitate with alcohol or ether the capsaicin and fats dissolve, whilst the bulk of the barium salts are insoluble. These operations, by eliminating the dextrin and fatty acids, effect a great reduction in the bulk of material to be handled.

The following are the details of this part of the isolation process which the authors have applied to numerous samples of extract of West African capsicums kindly prepared for them by Messrs. James Woolley, Sons and Co., of Manchester.

The extract (450 grams) is mixed with hot water (900 c.c.) and ammonia (25 c.c.; D 0·880) previously diluted with several times its bulk of cold water. On stirring, the whole forms an apparently homogeneous solution; it is heated on the water-bath and 90 grams of finely powdered hydrated barium chloride are sifted in very slowly with constant stirring. At this stage the liquid, which contains much brown, semi-fluid deposit, and should have a strong odour of ammonia, is allowed to cool and is separated mechanically from the bulk of the insoluble deposit, filtered, and extracted with ether. The ether is further utilised to extract the deposit, although the latter is subsequently washed several times with fresh ether in order to secure the whole of the contained capsaicin. The united ethereal extracts are evaporated and provide usually about 50—80 grams of "concentrated extract" of capsaicin.

The most satisfactory method of proceeding to the isolation of capsaicin from this "concentrated extract" is to subject it at once to treatment with methyl-alcoholic barium hydroxide in order to

destroy impurities of fatty nature. For this purpose the extract is
dissolved in several times its weight of methyl alcohol, the solution
heated to boiling, and finely powdered barium hydroxide sifted in at
intervals until the solution remains alkaline without further addition
after several hours' boiling. Glacial acetic acid is now added cauti-
ously until the solution has permanently lost all alkalinity (towards
phenolphthalein), when the methyl alcohol is removed by distilla-
tion. The residue is now extracted repeatedly with dry acetone, and
the latter recovered by evaporation, when the residue contains prac-
tically the whole of the capsaicin which was present in the original
extract. A repetition of the last process of extraction with dry
acetone is perhaps as a rule desirable, as the whole success of the
application of this solvent for the removal of barium salts depends
on the exclusion of moisture, which is not easy to secure in the first
operation.

The residue still contains traces of impurities of both neutral and
acid character. It is subjected to treatment similar to that applied
by Thresh to a much more impure material (*Pharm. J.*, 1876, [iii],
7, 260), that is to say, it is dissolved in aqueous sodium hydroxide
(5 per cent.), the solution extracted with ether to remove traces of
neutral material and then saturated with carbon dioxide, when the
precipitate is isolated by extraction with ether. The precipitate
yields capsaicin in crystalline form most readily by a device
also employed by Thresh and applied by the present authors as
follows:

Crude capsaicin (10 grams) is dissolved in aqueous sodium hydr-
oxide (100 c.c. of 2 per cent.) and warmed on the water-bath until
the temperature is about 60°. A warm saturated solution of am-
monium chloride is then gradually added until a permanent tur-
bidity is produced. On cooling, crystalline capsaicin is deposited,
and may be collected. The mother liquor is again treated with
ammonium chloride solution until the deposition of capsaicin ceases.

Properties of Capsaicin.

Many of the more evident properties of capsaicin have already
been described by previous workers, and in view especially of the
accurate descriptions given by Micko (*loc. cit.*) and Nelson (*loc. cit.*)
only a few additional notes are necessary here.

The most highly purified specimens of capsaicin melted at 64—65°.
The substance appears to be optically inactive; a solution containing
1·2146 grams dissolved in benzene and made up to 20 c.c. showed no
appreciable rotatory power in a 2-dcm. tube at 15°.

Analyses of several pure samples were carried out: Found: $C = 71.02$, 70.97, and 70.88; $H = 8.90$, 8.85, and 9.01; $N = 4.7$.

$C_{18}H_{27}O_3N$ requires $C = 70.82$; $H = 8.85$; $N = 4.6$.

$C_{18}H_{28}O_3N$,, $C = 70.59$; $H = 9.15$; $N = 4.6$.

$C_{18}H_{29}O_3N$ requires $C = 70.35$; $H = 9.44$; $N = 4.6$ per cent.

For the determination of hydroxyl, 0.2437 gram was treated with magnesium methyl iodide in amyl ether, 23.2 c.c. of methane were evolved at $70°$ and 770 mm.; whence $OH = 5.3$, the theoretical percentage being 5.6.

Capsaicin is sparingly soluble in concentrated hydrochloric acid, and the saturated solution deposits it in crystals on the addition of water. It is scarcely affected when boiled for several hours with 50 per cent. aqueous sodium hydroxide, but is appreciably decomposed after several hours' heating with concentrated hydrochloric acid.

Methylcapsaicin, $C_{17}H_{23}ON(O\cdot CH_3)_2$.

This compound is prepared by dissolving capsaicin and methyl sulphate in methyl alcohol and then slowly adding excess of a solution of sodium hydroxide while the whole is kept cool. After half an hour or more the bulk of the solvent is removed, the neutral methylcapsaicin separated from the residual aqueous solution by filtration or by extraction with ether, washed, and crystallised from dilute alcohol.

Found: $C = 71.39$; $H = 9.16$.

$C_{19}H_{29}O_3N$ requires $C = 71.47$; $H = 9.09$ per cent.

Methylcapsaicin dissolved readily in most of the ordinary organic media with the exception of cold light petroleum; it is insoluble in water or alkali hydroxides. It crystallises from dilute alcohol in slender, silky needles melting at $74°$, and is much less pungent than capsaicin.

This derivative appears to be slowly altered by boiling with acetyl chloride and it reacts with phosphorus pentachloride below $100°$, yielding an oil containing nitrogen, which is volatile in steam and has an odour suggesting that of many nitriles. The authors propose to study the products of this reaction in greater detail in the near future. Methylcapsaicin does not appear to react with phenylhydrazine, and it is recovered unaltered after prolonged boiling with alcoholic hydroxylamine acetate.

Reduction of Capsaicin.

Both capsaicin and its methyl ether are attacked by many comparatively mild reducing agents, but, as a rule, imperfectly. Am-

monia is always one of the products of change, but methylamine has never been detected even in traces. Numerous experiments have been made with the object of identifying the main products, but owing to the small quantities of capsaicin attacked the results were not very decisive. In one experiment, however, 10 grams of capsaicin were treated with a very large excess of metallic sodium in boiling alcohol; the dissolved sodium was precipitated from the resulting solution as carbonate with the aid of a stream of carbon dioxide and the bulk of the solvent removed by distillation through an efficient still-head. Ammonia, free from all traces of methylamine, passed over with the alcohol. From the residue in the still there was isolated without great difficulty nearly half of the capsaicin originally taken and also a small quantity of a liquid, volatile in steam, having a somewhat fragrant odour of higher fatty alcohols. The bulk of this liquid boiled at about 216—217°. As the quantity obtained did not admit of purification for analysis the fraction 216—217° was oxidised by means of dichromate and sulphuric acid mixture; the resulting fatty acid was extracted with ether, boiled with thionyl chloride, and the product shaken with concentrated aqueous ammonia. The amide of the acid was obtained in this way, and after recrystallisation from water appeared as silvery leaflets melting at 98—100°.

Oxidation of Methylcapsaicin with Potassium Permanganate.

Pure methylcapsaicin (10 grams) was dissolved in 3 litres of acetone and finely powdered potassium permanganate was very gradually added until a permanent pink tinge persisted in the solution—this operation occupied about two days—the temperature of the solution never being allowed to exceed 25°. The manganese dioxide was filtered off and washed repeatedly with acetone, the washings being added to the main filtrate and then evaporated.

The residue so obtained, which consisted of a viscid, reddish-brown, semi-solid oil, was subjected to steam distillation from acid solution. The distillate contained a very small quantity of a fatty acid, which was isolated in the usual manner; it was converted into its amide and gave a crystalline product, which melted at 98—99° and was apparently identical with that obtained from the oxidation of the alcohol referred to in the previous experiment, but the yield was extremely small and did not amount to more than 0·05 gram.

The residue, non-volatile in steam, was rendered alkaline with sodium carbonate and then extracted with ether. The ethereal solution yielded slightly more than 5 grams of unchanged methylcapsaicin. The sodium carbonate solution after removal of the methyl-

capsaicin gave nearly 2 grams of an acid, which readily crystallised from hot water in hard, flat needles melting at 179—180°. This acid yielded a chloride melting at 69° and an amide melting at 163°. Veratric acid, chloride, and amide melt at 70° and 164° respectively, and when mixed with the above products from methylcapsaicin were unchanged in melting point. The acid was dried in the steam-oven and analysed. (Found, $C=59.4$; $H=5.4$. $C_9H_{10}O_4$ requires $C=59.3$; $H=5.5$ per cent.)

There is therefore no doubt that the acid was veratric acid.

Oxidation of Methylcapsaicin with Chromic Acid.

Methylcapsaicin was oxidised by a boiling solution of chromic acid in dilute sulphuric acid. The liquid was then subjected to a current of steam and oily drops passed over. The whole of the distillate was rendered alkaline with sodium carbonate and evaporated almost to dryness; it was then carefully acidified and an oily acid was liberated which was extracted with ether. The product had a strong odour of acetic acid and was therefore exposed over solid potassium hydroxide in a desiccator for several days. The odour of the acetic acid disappeared and gave place to a rather pleasant one recalling that of *n*-nonoic acid. The colourless oil ultimately obtained was cooled in ice-water, when it readily solidified to a crystalline mass which melted sharply at 12° (nonoic acid melts at 12.5°). It also yielded an amide melting at 98—99°, which was in no respect distinguishable from the amide of *n*-nonoic acid prepared from the pelargonic acid of commerce.

The investigation is being continued.

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    MANCHESTER.   [*Received, July 25th,* 1919.]

NOTE.—Since the work recorded in the foregoing pages was completed, the authors' attention was called to the paper by Nelson (*J. Amer. Chem. Soc.*, 1919, **61**, 1115), which renders certain of their previous views obsolete.

Inter alia, Nelson has obtained from capsaicin by the action of acids and alkalis under pressure vanillylamine and a decylenic acid, the latter having a branched chain. He concludes that capsaicin is a condensation product of vanillylamine and a decylenic acid.

The present authors at first suspected that the fatty acid repeatedly referred to in their own communication was identical with this decylenic acid. They obtained their acid in very small

quantities, and the quantity of amide available for a combustion was only 0·0921 gram (Found, C = 68·7; H = 12·3. $C_9H_{19}ON$ requires C = 68·8; H = 12·1 per cent.), whilst its properties as well as those of its amide closely resembled those of n-nonoic acid; thus when super-cooled the acid at once solidified when seeded with n-nonoic acid, and the amide, as already mentioned, could not be distinguished by appearance or by a mixed melting-point determination from the amide of n-nonoic acid.

Since the authors' attention was called to Nelson's work, the supposed nitrile obtained directly from methylcapsaicin by the action of inorganic acid chlorides has successfully been converted by means of hydrogen peroxide and dilute sodium hydroxide at 40° into an acid amide melting at 98—100°.

The present authors are not fully disposed to accept Nelson's view of the constitution of capsaicin as final. His conception of capsaicin as an acid amide is not easily reconciled with the somewhat ready reduction of a part of capsaicin to ammonia and an aliphatic alcohol boiling at about 216—217°; its distinctly basic character and the great stability of the substance towards alkalis are also somewhat difficult to understand. They originally hazarded the view that capsaicin was probably a derivative of dihydro-oxazole, and the possibility is not wholly excluded that capsaicin is built with a ring structure such as

$$ \text{HO} \underset{CH_3 \cdot O}{\overset{}{\diagdown}} \text{-CH} \underset{O}{\overset{NH \cdot CH}{\diagup}} C \cdot C_8 H_{17}, $$
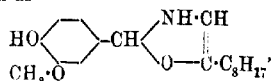
for under the energetic conditions used by Nelson internal oxidation or molecular rearrangement would not be surprising.

XCVIII.—The Vapour Pressures and Densities of Mixtures of Acetone and Methyl Ethyl Ketone.

By TUDOR WILLIAMS PRICE.

MUCH work, both theoretical and practical, has been done on the vapour pressures of binary mixtures, notably by Duhem, Lehfeldt, Ostwald, Roozeboom, Zawidski, and Young. It has been shown that for binary mixtures the components of which are miscible in all proportions, the vapour pressure at any one temperature may lie between those of the components; it may be higher or lower than that of either component.

If, however, the two components are closely related, the curvature f the graph, representing the relation between vapour pressure and oncentration for any particular temperature, should not be great. According to Guthrie (*Phil. Mag.*, 1884, [v], **18**, 517), if there is o heat or volume change on mixing the two components, the relation between vapour pressure and percentage composition by weight, expressed graphically, should be a straight line, but this does not enerally hold.

Van der Waals (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, , 170) considers that, if the critical pressures of the two substances re equal or nearly so, and if the molecular weight of each is ormal in both the liquid and gaseous states, and if the relation iggested by Galitzine and by Berthelot holds good, that is, if $._2 = \sqrt{a_1 \cdot a_2}$, where $a_1 ._2$ represents the attraction of the unlike olecules, and a_1 and a_2 the attraction of the like molecules, then ie relation between the vapour pressure and molecular composition ould be represented by a straight line, that is,

$$P = \frac{p \cdot P_A + (100 - p)P_B}{100},$$

there P, P_A, and P_B are the vapour pressures of the mixture and he two components A and B at the same temperature, and p is the iolecular percentage of liquid A in the mixture.

This relation has been verified many times, notably by Young, or mixtures such as chlorobenzene and bromobenzene, which are losely related. When the components are very closely related, ut have different critical pressures, the percentage difference etween the observed and calculated pressures $\frac{100\ P' - P}{P}$ for the

iixtures at any temperatures is very small, even when there is iolecular association in the liquid state, as with methyl and ethyl lcohol.

During the course of experiments on the production of cordite, sing methyl ethyl ketone as substitute in whole or in part for cetone as the gelatinising agent, it was found that some abnormalities were obtained in the volatility of the samples. For example, cordite gelatinised by a mixture of equal proportions by weight f acetone and methyl ethyl ketone had a lower volatility than ordite made with acetone or with methyl ethyl ketone. This iowed that the cordite gelatinised with the mixed solvent dried uicker than the others, presumably owing to the fact that the) per cent. mixture of acetone and methyl ethyl ketone has a reater vapour pressure than either of its two components.

This supposition, although unlikely because of the close relation-

ship between acetone and methyl ethyl ketone, is not outside the bounds of possibility, owing to the great difference between the critical pressures, which are given as 52·2 and 60·0 atmospheres for acetone (Sazotschewsky, in Landolt and Bornstein's "Tabellen') and 47·5 atmospheres for methyl ethyl ketone (Grassi, *Nuovo Cim.*, 1914, [vi], **7**, i, 313).

It was recognised that vapour-pressure measurements of the pure solvents and their mixtures would not furnish an absolute guide to the rate of escape of solvent from cordite on drying, because of the colloidal nature of the latter, but it was thought that such measurements would throw some light on the abnormal behaviour of cordite made with mixed solvent when being dried. Accordingly, a series of vapour pressure determinations were carried out, the results of which are given below.

EXPERIMENTAL.

Materials.—The acetone was prepared from commercial acetone as follows. After drying and fractionation, it was treated with sodium iodide according to Shipsey and Werner's method (T., 1913, **103**, 1255). The white, needle-shaped crystals of the addition compound, $NaI,3C_3H_6O$, were quickly collected, pressed between blotting-paper, and transferred to a dry distilling flask. On gently warming, the acetone distilled over. The distillate was dried over fused calcium chloride for twenty-four hours and distilled through a five-bulb column. The fraction 56·15—56·25°/760 mm. was collected separately, dried again over fused calcium chloride for twenty-four hours, and fractionated as before. Practically all distilled constantly at 56·2°/760 mm. (corr.).

A sample gave the following results on analysis:

Acidity as CO_2	= 0·0012 per cent.
„ „ acetic acid	= Nil.
Alkalinity as $N/10\text{-}H_2SO_4$ c.c.	= Nil.
Turbidity with water	= Nil.
Residue on evaporation	= 0·0003 per cent.
Permanganate test	= 50 minutes.

The methyl ethyl ketone was freed from acetone by two washings with saturated brine, in which it is not very readily soluble. The purified ketone was dried over fused calcium chloride and fractionated through a five-bulb column. The fraction distilling at 78—80° was dried and fractionated again. From this second distillation, a fraction boiling at 79—80° was collected separately, dried

l again fractionated. In this way, a final fraction was obtained ling at 79·5—79·6°/759 mm. (corr.). The boiling point of thyl ethyl ketone is given as 79·57°/760 mm. (Marshall, T., 1906, , 1375).

A sample gave the following tests on analysis:

Aldehydes.................................... = Nil.
Acidity as CO_2............................ = 0·0002 per cent.
Alkalinity as $N/10\text{-}H_2SO_4$ c.c. .... = Nil.
Permanganate test .... = 20 minutes.

The liquids were kept in tightly stoppered bottles in a dark cup-ird.

Apparatus.—The apparatus used was designed by Mr. Allan rton (private communication).

t consisted of two similar barometer tubes connected at the tom by a T-piece to each other and to a mercury reservoir, ich could be raised or lowered at will. The top of each tube s sealed to a piece of capillary tube, longer than the barometer e, which was bent over parallel to the barometer tube to which was sealed. The bottom of each capillary tube was bent over in and dipped into small cups of mercury.

he barometer tubes were surrounded by a wide glass tube con-ning water, which was circulated and stirred by compressed air l kept at a constant temperature.

he method of procedure was as follows. Recently boiled cury was placed in the reservoir, which was then raised until mercury filled the barometer tubes and the capillaries and over-wed into the cups. The reservoir was then lowered and the rcury column broke at the junction of the capillaries with the rometer tubes, thus forming a vacuum in the latter. This was eated until no air was left in the tubes and a perfect vacuum tained.

The liquid the vapour pressure of which was to be measured was n placed above the mercury in one of the small cups. The rcury reservoir was raised until mercury overflowed into the ps. The cup with the liquid was then moved until the end of capillary was in the liquid above the mercury. On lowering reservoir, some of this liquid was drawn into one of the baro-ter tubes. By this means, the latter contained the necessary uid and its vapour, whilst the other tube acted as a barometer.

A slight modification was found to be necessary for accurate rk. As described by Morton, the capillary tubes are outside the ter-jacket, and are consequently at a lower temperature than the ervation tube. Liquid from the observation tube therefore

distils over and condenses above the mercury in the capillary tube, thus causing an appreciable alteration of the concentration in the case of a mixture. This difficulty was overcome by making the water-jacket wider, so as to contain the capillary tubes and to keep them at the same temperature as the observation tube.

Two thermometers were used in the work, one reading from 0° to 50° in tenths, and the other from 50° to 100° in tenths. These were carefully standardised by comparison with thermometers which had recently been tested at the National Physical Laboratory, and could easily be read to 0·01°. The temperature of the water surrounding the observation tubes was kept constant to within 0·05°, and all readings of the mercury and solvent levels were taken through a cathetometer.

A quantity of liquid remained in the observation tube above the mercury, and for this a correction had to be applied, obtained from the densities of the mixtures at the required temperature.

The densities were determined in a Regnault specific gravity bottle for liquids, of about 50 c.c. capacity, fitted with a capillary stem widening out into a cup-shaped reservoir fitted with a ground-glass stopper. All weighings were done on a balance sensitive to 0·0001 gram with standardised brass weights, and in the neighbour-hood of 760 mm. pressure, and hence no correction was made for changes in atmospheric pressure. The balance case was kept dry by means of dishes containing calcium chloride, so that no correction was made for the relative humidity of the air.

A counterpoise of the same kind of glass and of the same shape as the specific gravity bottle was used in all weighings, and all weights were reduced to a vacuum.

The thermostat was provided with a thermoregulator and mechanical stirrer, and could be kept at the desired temperature within 0·05°.

For the pure liquids, determinations were made in duplicate; these agreed very closely, and the mean is given. For the mixtures, determinations were carried out in duplicate on the same solution, there being not sufficient material to make up two separate solutions of the same concentration.

Results.—The vapour pressures obtained are given in table I. Each figure is the mean of three or four determinations at the same temperature, which agreed very closely.

TABLE I.

Vapour Pressures of Mixtures of Acetone and Methyl Ethyl Ketone at Various Temperatures.

Composition of mixture.

Percentage of acetone by weight.	Molecular percentage of acetone.	Vapour pressure in mm. at following temperatures.						
		$20°$	$25°$	$30°$	$35°$	$40°$	$45°$	$50°$
100	100	186·3	232·0	284·6	348·1	425·3	510·8	620·9
75	78·83	167·8	—	255·5	—	379·1	—	548·2
62·5	67·42	161·8	—	243·3	—	354·0	—	508·4
50	55·38	155·5	—	226·5	—	327·8	—	469·7
37·5	42·69	141·3	—	205·8	—	299·6	—	430·2
25	29·27	125·5	—	183·5	—	267·4	—	388·1
12·5	15·06	109·9	—	160·6	—	234·2	—	341·9
0	0	77·5	98·4	121·4	151·0	188·4	252·9 (at 46·5°)	300·0

These results are shown graphically in Figs. 1 and 2. Fig. 1 shows the relation between vapour pressure and concentration (by weight) over the whole range from pure acetone to pure methyl ethyl ketone at the temperatures indicated, whilst Fig. 2 shows the relation between vapour pressure and temperature for the pure substances and all the mixtures.

The densities are given in table II.

TABLE II.

Densities of Mixtures of Acetone and Methyl Ethyl Ketone at Various Temperatures.

Composition of mixture.

Percentage of acetone by weight.	Molecular percentage of acetone.	Density at following temperatures.			
		$20°/4.°$	$30°/4°.$	$40°/4°.$	$50°/4°.$
100	100	0·79082	0·77931	0·76784	0·75599
75	78·83	0·79428	0·78311	0·77181	0·76020
62·5	67·42	0·79603	0·78495	0·77368	0·76233
50	55·38	0·79782	0·78677	0·77567	0·76439
37·5	42·69	0·79956	0·78869	0·77776	0·76664
25	29·27	0·80135	0·79061	0·77982	0·76877
12·5	15·06	0·80314	0·79249	0·78173	0·77084
0	0	0·80495	0·79442	0·78391	0·77315

Discussion of Results.—The accuracy of the results obtained in the vapour pressure measurements may be gauged by comparing them with results obtained by other workers. Table III affords a comparison of the various results given for acetone.

TABLE III.

*Showing Results obtained for the Vapour Pressure of Acetone
by Various Workers.*

Vapour pressure of acetone in mm. of mercury.

Temperature	Author.	Regnault.[1]	Sameshima.[2]	Taylor.[3]
20°	186·3	179·6	184·8	182·5
25	232·0	—	229·2	229·0
30	284·6	281·0	282·7	281·0
35 ·	348·1	—	346·4	343·0
40	425·3	420·2	421·5	416·0
45	510·8	—	510·5	505·0
50	620·9	620·9	612·5	607·0

[1] Obtained from Landolt and Bornstein's "Tabellen."
[2] *J. Amer. Chem. Soc.*, 1918, **40**, 1482.
[3] *J. Physical Chem.*, 1900, **4**, 436.

The agreement between the present results and those of Sameshima is good, except at 50°, at which temperature better agreement is obtained with ·Regnault.

The results show, however, that the apparatus is capable of giving accurate results, and does away with the necessity of using stopcocks, with their attendant troubles due to leakiness and the presence of grease. The chief source of error is the possibility of the liquid absorbing air before being carried over into the observation tube. With pure liquids, this possibility can be obviated to a large extent by boiling immediately before introduction, but with mixtures this procedure would alter the concentration, and hence the above possibility must not be neglected.

As regards methyl ethyl ketone, no figures have been found in the literature for the vapour pressure at temperatures between 20° and 50°.

An examination of Fig. 1 shows that the vapour pressure-concentration curves lie between the vapour pressures of the two components at all temperatures, thus negativing the suggestion that there might be a mixture of acetone and methyl ethyl ketone having a higher vapour pressure than either component. Hence the explanation of the abnormality of the volatility of cordite gelatinised with a mixture of equal parts of acetone and methyl ethyl ketone, based on the above suggestion, is unfounded.

The graphs in Fig. 1 are not straight lines, but they approximate thereto, and this approximation is nearer as the temperature is increased. The deviation from a straight line, for the curve at 50°, is given in table IV by comparing the observed vapour pressures of the mixtures with those calculated according to the expression

$$P = \frac{m \cdot P_A + (100 - m)P_R}{100},$$

where m is the molecular percentage of acetone in the mixture and P_A and P_B are the vapour pressures of acetone and methyl ethyl ketone respectively. P' is the observed vapour pressure of the mixture and $\dfrac{(P - P')}{P'}100$ is the percentage difference.

Fig. 1.

Showing relation between vapour pressure and composition (by weight) of mixtures of acetone and methyl ethyl ketone

Curve   I. at 20° | Curve III. at 40°
  ,,   II. ,, 30 | ,,   IV. ,, 50
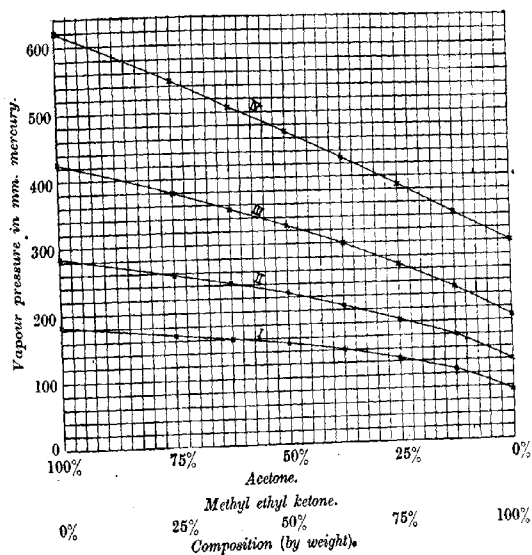
TABLE IV.

Difference between Observed and Calculated Vapour Pressures of Mixtures of Acetone and Methyl Ethyl Ketone at 50°.

Molecular percentage of acetone = m.	Observed v.p. in mm. of Hg$=P'$.	Calculated v.p. in mm. of Hg $= P$.	$\dfrac{100\,(P - P')}{P'}$.
78·83	548·2	553·0	+0·88
67·42	508·4	516·3	+1·55
55·38	469·7	477·7	+1·70
42·69	230·2	437·0	+1·58
29·27	388·1	393·9	+1·50
15·06	341·9	348·3	+1·87

The maximum deviation is about 1·9 per cent. In Fig. 2, the curves have the familiar shape associated with vapour pressure-temperature curves, and when the logarithms of vapour pressure are plotted against temperature for each mixture and for the pure solvents, the resulting graph is practically a straight line.

There is a considerable difference in the figures given in the

FIG. 2.

Showing relation between temperature and vapour pressure for mixtures of acetone and methyl ethyl ketone.
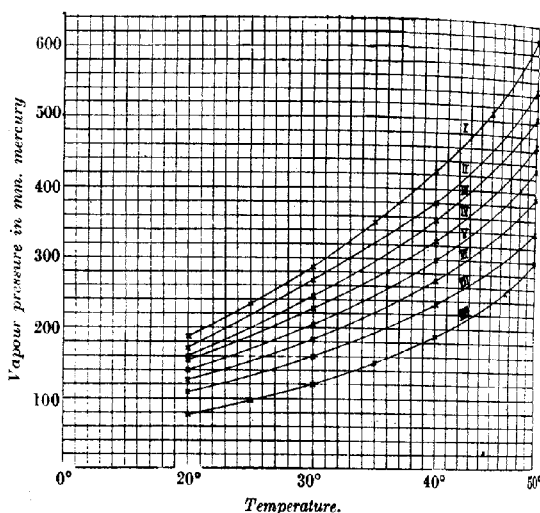
Curve	I. = Acetone.	Curve	V. = 37½% Acetone (by wt.)
,,	II. = 75% Acetone (by wt.)	,,	VI. = 25 ,, ,, ,,
,,	III. = 62½% ,, ,, ,,	,,	VII. = 12½% ,, ,, ,,
.,	IV. = 50% ,, ,, ,,	,,	VIII. = 100% Methyl ethyl ketone.

literature for the density of acetone. Thus Perkin (T., 1884, **45**, 478) gives D_{15}^{15} 0·79652, which is equivalent to D_4 0·79072.

Linnemann (T., quoted by Perkin) gives D_{15}^{15} 0·7975 or D_4^{20} 0·79170. Perkin's value is considerably lower, and was obtained with acetone purified by the sodium hydrogen sulphite method and boiling at 55·6—55·9°. McElroy and Krug (*J. Soc. Chem. Ind.*, 1893, **12**, 177) give D_4^0 0·79197. Squibb (*J. Amer. Chem. Soc.*, 1895, **17**, 200) gives D_{15}^{15} 0·7966 or D_4^{20} 0·7908. This value agrees closely with that obtained by Perkin. Bramley (T., 1916, **109**, 455) obtained

he value D_4^{20} 0·7912. Thus the range of published figures varies rom 0·79072 to 0·79197 for the density of acetone at 20°/4°. The esult obtained in the present work is the mean of two which agreed xactly, namely, 0·79082. The specific gravities in this work are iven to five decimal places, by which is meant that they are orrect to four places, the fifth figure being doubtful in each case. t will be seen, therefore, that excellent agreement is obtained with he result of Squibb (D_4^{20} 0·7908) and with that of Perkin D_4^{20} 0·79072).

The results for the density of acetone at other temperatures igree well with those obtained by Bramley (*loc. cit.*), as shown in he following table.

TABLE V.

Comparison of Results for Density of Acetone at Various Temperatures.

	Density.	
Temperature.	Author.	Bramley.
2C°/4°	0·79082	0·7912
30°/4°	0·77931	0·7793
40°/4°	0·76784	0·7674
50°/4°	0·75599	0·7555

The density of methyl ethyl ketone is given by Marshall (T., 906, **89**, 1376) as 0·81005 at 15°/4°. Extrapolation from the esults obtained by the present author gives 0·8101, which agrees rery well with Marshall's figure.

The density–concentration curves are all straight lines parallel o each other, thus showing that there is no contraction or ixpansion in volume on mixing acetone and methyl ethyl ketone it any of the temperatures 20° to 50°.

The density–temperature curves for the pure liquids and for the mixtures are also practically straight lines, the curvature being ixtremely slight. For acetone, the difference in density per degree ïver the whole range is 0·001161, and for methyl ethyl ketone it is Ô·00106.

Summary.

Vapour pressures and densities of acetone, methyl ethyl ketone, ind mixtures of the two have been determined from 20° to 50°.
The vapour pressure–concentration curves all lie between the ïapour pressures of the components, there being no sign of a iaximum at any point.
The density–concentration curves are straight lines, showing that

U U*

no change in volume occurs when acetone and methyl ethyl ketone are mixed in any proportions from 20° to 50°.

Organic Chemistry.

The Preparation of some True Acetylenic Hydrocarbons ' means of Monosodioacetylene. Picon (*Compt. rend.*, 1919,]9, 32—34. Compare this vol., i, 246).—Normal amyl iodide lcts with monosodioacetylene in liquid ammonia, yielding ptinene, together with a small amount of β-methyl-Δ^α-butene, the lter due probably to the presence of a small amount of active lyl iodide in the sample used.

Normal primary octyl iodide in the same way yields *decinene*, p. 59°/13 mm., m. p. −40°, D_0^0 0·791, and hexadecyl iodide gives ttadecinene, m. p. 22·5°, D_0^0 0·8696.   W. G.

Carbon Tetrachloride, Chloroform, and Carbon Hexa-loride from Natural Gas. G. W. Jones and V. C. Allison , *Ind. Eng. Chem.*, 1919, **11**, 639—643).—Natural gas rich in lthane or ethane, such as that of Pittsburgh, can be used for the)duction of carbon tetrachloride, chloroform, and carbon hexa-loride. For this purpose, it is passed, together with a slight 1ess of chlorine, through a tube which contains a suitable catalyst, 1 is heated in an electric furnace. The most suitable catalysts 1 war-gas charcoal, "bachite" (a patent carbon material), and amed anthracite coal, all of which have a high absorptive lacity for chlorine. The reaction begins at 250° and increases intensity up to about 500°, above which the catalyst is attacked 1 carbon is deposited. One litre of natural gas (90% of methane 1 10% of ethane) when completely chlorinated should yield 1 c.c. of chlorination products. Methane is less readily orinated than higher saturated hydrocarbons. By introducing gas at the rate of 1 litre per hour, methane is completely con-ted into carbon tetrachloride and ethane into carbon hexa-)ride. By increasing the rate of introduction of the natural gas,)roform is obtained in addition to carbon tetrachloride. [See > *J. Soc. Chem. Ind.*, 1919, 599a.]   C. A. M.

Preparation of Tetrachloroethylene. H. B. Weiser and E. Wightman (*J. Phys. Chem.*, 1919, **23**, 415—439).—The limum temperature for the thermal decomposition of carbon tachloride into chlorine and tetrachloroethylene lies between]0° and 1400°, but a certain amount of decomposition occurs at lperatufes as low as 600°. In order to minimise the further ction of chlorine on tetrachloroethylene to form solid hexa-)roethane, the products of decomposition must be cooled as idly as possible, and may with advantage be diluted with an rt gas such as air or nitrogen. The decomposition is con-jently conducted in an electrically heated quartz tube, and an I condenser may be used provided that the condensing surface

is kept dry and comparatively cool. [See also *J. Soc. Chem. Ind.*, 1919, September.]

G. F. M.

The Catalytic Formation of Alkyl Chlorides from Primary Alcohols. PAUL SABATIER and A. MAILHE (*Compt. rend.*, 1919, 169, 122—125).—When the vapours of primary alcohols of the methyl series are passed along with hydrogen chloride over aluminium oxide at 420°, the corresponding primary alkyl chloride, together with some secondary or tertiary chloride and some ethylenic hydrocarbon, is obtained. In this way, propyl alcohol gives a mixture of propyl and *iso*propyl chlorides, the latter predominating; *iso*butyl alcohol gives a mixture of *iso*butyl chloride, CHMe₂·CH₂Cl, and the tertiary chloride, CMe₃Cl, in the proportion of 1:3; *iso*amyl alcohol gives a mixture of the primary, secondary, and tertiary chlorides in the proportion of 1:2:3, and heptyl alcohol gives heptene and a mixture of primary and secondary heptyl chlorides, together with a little diheptene.

W. G.

The Spontaneous Oxidation of Organic Complexes of Cobalt. H. COLIN and O. LIÉVIN (*Compt. rend.*, 1919, 169, 188—190).—Alkaline solutions of certain organic substances in the presence of cobalt sulphate undergo spontaneous oxidation in the air. In some cases, the amount of oxidation is limited, whilst in others it increases with the time. Glycerol and lactic acid furnish examples of the first type, whilst dextrose, mannitol, erythritol, and tartaric acid are examples of the second class of organic substances. As explanation of this phenomenon, the authors suggest that the cobalt, in the presence of alkali, forms true complexes with the organic compounds. These complexes oxidise spontaneously and turn green, the organic substance being attacked at the same time. If the products of this secondary oxidation are capable of reducing the green complex, there is a continuous transportation of oxygen, but if not the absorption is limited.

W. G.

Action of Chlorosulphonic Acid on Methyl Hydrogen Sulphate. R. LEVAILLANT and L.-J. SIMON (*Compt. rend.*, 1919, 169, 140—143).—Methyl hydrogen sulphate reacts with chlorosulphonic acid to give methyl chlorosulphonate according to the equation $OH·SO_2Cl + OH·SO_2·OMe \rightleftharpoons SO_2Cl·OMe + H_2SO_4$. This reaction is, however, reversible, and an equilibrium is set up. At the same time, a secondary reaction proceeds between some of the methyl chlorosulphonate formed and some of the unchanged methyl hydrogen sulphate, this reaction also being reversible:

$SO_2Cl·OMe + OH·SO_2·OMe \rightleftharpoons SO_2Cl·OH + SO_2(OMe)_2$.
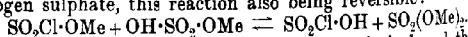
As a result of the balance of these reactions, it is found that the yield of methyl chlorosulphonate is only about half of the theoretical yield. *Methyl chlorosulphonate* is a colourless liquid and a violent lachrymator. It has b. p. 42°/16 mm., 134—135°/760 mm., D⁰ 1·514, D¹⁵ 1·492, n_D^{17} 1·414.

W. G.

Action of Chlorosulphonic Acid on Methyl Sulphate. Preparation of Methyl Chlorosulphonate. R. LEVAILLANT and L.-J. SIMON (*Compt. rend.*, 1919, **169**, 234—236. Compare preceding abstract).—When heated together, methyl sulphate and chlorosulphonic acid react according to the equation

$$SO_2Cl\cdot OH + Me_2SO_4 \;\rightleftharpoons\; SO_2Cl\cdot OMe + OH\cdot SO_2\cdot OMe,$$
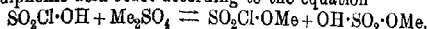
which is, however, reversible. Further, the methyl hydrogen sulphate formed, in its turn, reacts with the chlorosulphonic acid, as already seen. The yield from methyl sulphate is 70% of theory, and may be increased if the product is fractionally distilled, giving two fractions, A, containing methyl chlorosulphonate and a little chlorosulphonic acid, and B, containing chlorosulphonic acid, methyl chlorosulphonate, and methyl sulphate, this second fraction B being added to further quantities of the original reacting mixture. W. G.

Preparation of the Fluorides of Organic Acids by means of Fluorosulphonic Acid and Fluorosulphonates. WILHELM TRAUBE and ANNA KRAHMER (*Ber.*, 1919, **52**, [*B*], 1293—1298).— The preparation of aliphatic acid chlorides by the action of heat on mixtures of salts of chlorosulphonic acid and fatty acids has been described by the Badische Anilin- & Soda-Fabrik (D.R.-P. 146690); the authors have attempted to prepare the fluorides by a similar method, but the results are not completely satisfactory. The best yields, obtained with fatty aromatic acids, do not exceed 20% of that theoretically possible, whilst with the simple aliphatic acids the yields fall as low as 5%. The by-products include considerable amounts of acid anhydrides. Better results are obtained by heating mixtures of fluorosulphonic acid and the fatty acid in a platinum vessel. The following substances are described: β-*phenylpropionyl fluoride*, b. p. 96°/17 mm., which is only slowly decomposed by water; *phenylacetyl fluoride*, b. p. 88—89°/17 mm.; benzoyl fluoride, b. p. 156°; acetyl fluoride, b. p. 20·5°; propionyl fluoride, b. p. 44°; *chloroacetyl fluoride*, b. p. 74°; *dichloroacetyl fluoride*, b. p. 71—72°. H. W.

Certain Aliphatic Compounds with Numerous Side-chains. RICHARD WILLSTÄTTER and DANIEL HATT (*Annalen*, 1919, **418**, 148—160).—The authors have synthesised $\alpha\beta\gamma\delta$-tetramethylhexoic acid by way of the ester of the corresponding β-hydroxy-acid, the method employed consisting in union of a ketone and the ester of an α-halogenated aliphatic acid in presence of zinc (compare Reformatsky, A., 1887, 717; 1896, i, 128) or magnesium (compare Zelinsky and Gutt, A., 1902, i, 585). The synthesis in this way of ethyl β-hydroxy-$\alpha\beta$-dimethylvalerate from methyl ethyl ketone and ethyl α-iodopropionate occurs readily, but ethyl *iso*butyl ketone and ethyl α-iodopropionate yield, in addition to the ester of the β-hydroxy-acid, also that of the corresponding unsaturated acid. Hydrogenation of the latter in presence of platinum gives the $\alpha\beta\gamma\delta$-tetramethylhexoic acid, which in habit resembles phytol derivatives, without, however, being identical with

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any of these. The β-hydroxy-acid is converted by the action of 62%, or even more dilute, sulphuric acid into the highly stable γ-lactone, this behaviour being that exhibited by other alkylated αβ-unsaturated acids.

βγ-Dimethyl-δ-pentanone, obtained by boiling ethyl methylisopropylacetoacetate (compare van Romburgh, A., 1887, 232) with hydrobromic and glacial acetic acids, has b. p. 128—133·5°/719 mm. (van Romburgh gave 135—140°); its *oxime*, $C_{17}H_{15}ON$, is a colourless, viscous oil, b. p. 82—82·5°/10 mm., with an odour of peppermint. By sodium and alcohol, the ketone is reduced to *βγ-dimethyl-δ-pentanol*, $C_7H_{16}O$, which is a somewhat viscous liquid, b. p. 149—150·5°/719 mm., D_4^{21} 0·836. *δ-Iodo-βγ-dimethyl-pentane*, $C_7H_{15}I$, has b. p. 56—61°/11 mm., and smells like camphor.

Ethyl β-hydroxy-αβ-dimethylvalerate,

$$OH \cdot CMeEt \cdot CHMe \cdot CO_2Et,$$

prepared from methyl ethyl ketone and ethyl α-iodopropionate in presence of magnesium, is a liquid, b. p. 78—79·5°/10 mm.

Ethyl αβ-dimethyl-Δ^α-butenoate, $CMeEt \colon CMe \cdot CO_2Et$, prepared by heating the preceding ester with oxalic acid, is a mobile liquid, b. p. 64—66°/13·5 mm., D_4^0 0·927, with a pleasant odour and a vigorous reducing action on permanganate.

Ethyl β-hydroxy-αβγ-trimethylvalerate,

$$CHMe_2 \cdot CMe(OH) \cdot CHMe \cdot CO_2Et,$$
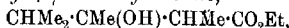
prepared from methyl isopropyl ketone and ethyl α-iodopropionate, is a mobile liquid, b. p. 90—93·5°/11·5 mm., $D_4^{17\cdot5}$ 0·977; it is not converted into the corresponding unsaturated ester by either oxalic acid, phosphoric oxide, or phthalic anhydride. The free *hydroxy-acid*, $C_8H_{16}O_3$, forms a viscous liquid, b. p. 136—140°/9·5 mm., and in a desiccator, or more rapidly on heating with dilute sulphuric acid (1:1), is converted into *αβγ-trimethyl-valerolactone*, $CHMe \!\! \overset{CMe_2-O}{\underset{CHMe \cdot CO}{<}}$, which crystallises in needles and lanceolate leaflets, m. p. 47·5°, b. p. 90·5—93°/10 mm., and has an intense menthol odour. When heated with hydriodic acid and phosphorus, the lactone gives an *alphyl iodide* (? octyl iodide), b. p. 164—167·5°, and a very stable *carboxylic acid* of high molecular weight, b. p. 272—279°/10 mm. When heated for a day at 160—210° with hydriodic acid (D 1·96), the lactone loses carbon dioxide and yields a saturated *hydrocarbon*, b. p. 84—89°, which smells like petroleum and appears to have the composition of a *cyclo*paraffin.

αβγδ-Tetramethyl-γ-hexolactone, $CHMe \!\! \overset{CMePr^\beta \cdot O}{\underset{CHMe-CO}{<}}$, is a somewhat viscous oil, b. p. 117—120°/12 mm., D_4^0 0·988, with an odour like that of menthol, and is only slowly oxidised by permanganate.

Tetramethyl-Δ^α-hexenoic acid, $CHMe_2 \cdot CHMe \cdot CMe \colon CMe \cdot CO_2H$, cannot be distilled even in a vacuum, owing to its ready conversion into the lactone, which forms slowly even at the ordinary tempera-

ture; the acid instantaneously combines with bromine and decolorises permanganate.

$\alpha\beta\gamma\delta$-*Tetramethylhexoic acid*, $CH_3\cdot[CHMe]_4\cdot CO_2H$, is a somewhat viscous, colourless oil, b. p. 136—136·5°/11 mm., $D_4^{20\cdot5}$ 0·935, and smells faintly like turpentine. Its *silver* salt was analysed.

T. H. P.

Transformation of Acid Salts of Dibasic Acids in Aqueous Solution. TH. SABALITSCHKA (*Ber.*, 1919, **52**, [*B*], 1378—1384).— Previous experiments by Thoms and Sabalitschka (A., 1917, i, 700) have shown that only minute traces of oxalic acid can be removed from aqueous solutions of potassium hydrogen oxalate by treatment with ether, this behaviour being in striking contrast with that observed with the acid salts of other dibasic organic acids. The author has therefore investigated the dialysis of solutions of potassium hydrogen oxalate of differing concentration and at differing temperatures. It is found that the diffusate invariably contains slightly more potassium in relationship to oxalic acid than is required for the acid salt, whilst the diffusing solution contains an excess of oxalic acid. It appeared probable that this is due to the existence of normal potassium oxalate and potassium tetroxalate in solutions of the hydrogen oxalate, and direct experimental evidence on this point is afforded by the crystallisation of potassium tetroxalate in the pure state from a not too concentrated solution of potassium hydrogen oxalate at +10°. Solutions of ammonium hydrogen oxalate do not appear to behave in a similar manner.

It is pointed out that oxalic acid can be completely volatilised at the temperature of the boiling-water bath, and, further, that commercial potassium hydrogen oxalate does not generally correspond with the formula KHC_2O_4.   H. W.

The Synthesis of Inositol Hexaphosphate and its Identity with the Phospho-organic Reserve Principle of Green Plants. S. POSTERNAK (*Compt. rend.*, 1919, **169**, 138—140. Compare this vol., i, 426).—Inositol hexaphosphate has been synthesised and isolated in the form of its double calcium sodium salt by heating inositol with phosphoric acid in the presence of phosphoric oxide at 120—130° for three hours. The crystallographic properties of this synthetic double salt have been examined, and on comparison with those of the double salt prepared from phytin, the two sets of measurements were found to be identical. The crystals are monoclinic [$a : b : c = 0.630066 : 1 : 0.639015$ and $\beta = 108°13'$]. This is taken as conclusive proof that the phospho-organic reserve principle of green plants is inositol hexaphosphate.

W. G.

Improvements Relating to the Preparation of Amines. WILLIAM RINTOUL, JOHN THOMAS, and NOBEL'S EXPLOSIVES CO., LTD. (Brit. Pat., 128372).—Secondary and tertiary amines

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are separated from mixtures of the two containing an excess of the latter by treatment with carbonyl chloride at temperatures below 25°, whereby the secondary amine is converted into a carb-amide chloride with the elimination of hydrogen chloride, which reacts, forming the hydrochloride of the tertiary amine. The reaction mixture is then treated with sufficient dilute hydrochloric acid to dissolve the whole of the tertiary amine, whilst the insoluble carbamide chloride is collected and boiled with either water or dilute hydrochloric acid to regenerate the secondary amine. In cases where the mixture of amines contains an excess of the secondary amine, the requisite excess of tertiary base is secured either by removing the secondary base in stages by repeating the above operation, or by actually adding a sufficient quantity of tertiary amine to the original mixture.　[See, further, *J. Soc. Chem. Ind.*, 1919, September.]　　　　　　　　G. F. M.

Preparation of Aminosulphonic Acids by the Aid of Salts of Fluorosulphonic Acid. WILHELM TRAUBE and ELISABETH BREHMER (*Ber.*, 1919, **52**, [*B*], 1284—1293).—The salts of fluoro-sulphonic acid possess the remarkable property of exchanging the fluorine atom for an amino-group when treated with an aqueous solution of the requisite base; under these conditions, a portion of the fluorosulphonic acid, greater or less according to the strength of the base, is hydrolysed to hydrofluoric and sulphuric acids, which represent the sole by-products of the change and which can readily be removed by chalk or barium hydroxide. The process has the considerable advantage over the older methods that it does not require the isolation of the base in the anhydrous condition. The following substances have been prepared in this manner: amino-sulphonic acid, aminoethylaminosulphonic acid, barium hydrazino-sulphonate, *potassium hydrazinosulphonate*, and *potassium methyl-aminosulphonate*, shining leaflets. *Methylaminosulphonic acid* forms long needles, m. p. 181°, and yields hygroscopic *ammonium* and *sodium* salts; the *barium* salt ($+ H_2O$) is stable in air; its *silver*, *copper*, and *lead* salts are freely soluble in water. The action of potassium nitrite on an aqueous solution of methylamino-sulphonic acid leads to the formation of *potassium methylnitroso-aminosulphonate*, $NO \cdot NMe \cdot SO_3K$, which, when reduced with zinc dust and acetic acid, and subsequently boiled with hydrochloric acid, gives methylhydrazine in 18% yield. Potassium ethylamino-sulphonate is formed from potassium fluorosulphonate and ethyl-amine; the corresponding free *acid* forms clusters of needles, m. p. 167—168°. *Propylaminosulphonic acid*, *isobutylaminosulphonic acid*, and *isoamylaminosulphonic acid* are similarly prepared, and have m. p.'s 172—173°, 192° (decomp.), and 188° respectively; the *potassium* salts are described. Phenylaminosulphonic acid is obtained in 38% yield. *Sodium methylhydrazinosulphonate* closely resembles the corresponding ethyl compound; it could not, however, be transformed into the diazomethanesulphonate by oxidation with mercuric oxide.　　　　　　　　　　　　　　　　H. W.

. aγ-**Amino-alcohols with Secondary Alcohol Function.**
ERNEST FOURNEAU and (MME.) PAULINE RAMART-LUCAS (*Bull. Soc.
Chim.*, 1919, [iv], **25**, 364—370).—Chloropropaldehyde readily
reacts with magnesium alkyl bromides or iodides to give the corre-
sponding secondary aγ-chloro-alcohols. These secondary alcohols
condense with amines, such as dimethylamine, to give the aγ-amino-
alcohols. The following compounds have been prepared.

a-*Chloropentan-γ-ol*, $CH_2Cl \cdot CH_2 \cdot CHEt \cdot OH$, b. p. 83—85°/
10 mm., 100°/60 mm., 173°/760 mm., giving an *acetyl* derivative,
1. p. 89°/15 mm., and a *benzoyl* derivative, b. p. 168°/15 mm.
-Iodopentan-γ-ol, b. p. 105—108°/15 mm., is obtained from the
chloro-alcohol by the action of sodium iodide. With dimethyl-
amine, a-chloropentan-γ-ol yields a-*dimethylaminopentan-γ-ol*, b. p.
75°/760 mm., 97°/46 mm. It gives a *hydrochloride* of its *benzoyl
ether*, m. p. 120—121°, and a *hydrochloride* of its p-*nitrobenzoyl
ether*, m. p. 145—146°. a-*Diethylaminopentan-γ-ol* has b. p. 76°/
3 mm., and yields the *hydrochloride* of its *benzoyl ether*, m. p.
106—107°, and the *hydrochloride* of its *methylcinnamyl ether*,
1. p. 136°.

a-*Chlorobutan-γ-ol*, $CH_2Cl \cdot CH_2 \cdot CHMe \cdot OH$, b. p. 70°/13 mm.,
gives a-*dimethylaminobutan-γ-ol*, b. p. 150°/760 mm., yielding the
hydrochloride of its *benzoyl ether*, b. p. 133—134°. a-*Diethyl-
aminobutan-γ-ol* has b. p. 72°/13 mm.

a-*Chlorohexan-γ-ol*, $CH_2Cl \cdot CH_2 \cdot CHPr \cdot OH$, b. p. 90—91°/
1 mm., 120°/35 mm., yields a-*dimethylaminohexan-γ-ol*, b. p.
193—194°/760 mm., giving the *hydrochloride* of its *cinnamyl ether*,
. p. 134—135°.

a-*Chloro-ζ-methylheptan-γ-ol*, b. p. 110—115°/13 mm.,
128—130°/25 mm., gives a-*dimethylamino-ζ-methylheptan-γ-ol*,
p. 120°/28 mm., yielding the *hydrochloride* of its *benzoyl ether*,
. p. 133—134°.

These chloro-alcohols, unlike those obtained from chloroacetone,
are obtained quite pure and are very stable to light.   W. G.

Carbamylglycollic Acids. ALFRED AHLQVIST (*J. pr. Chem.*,
19, [ii], **99**, 45—84).—With carbamic acid, hydroxy-acids yield
carbamates, for instance, $CO_2H \cdot CH_2 \cdot O \cdot CO \cdot NH_2$, which are at the
same time acids and urethanes, and are most suitably named
carbamic ester acids, the term urethane acids being better applied
to acids of the type $CO_2H \cdot CH_2 \cdot NH \cdot CO_2R$. Few of these carbamic
ester acids being known (compare Thiele and Dent, A., 1899,
i, 14; Lambling, A., 1898, i, 588; 1899, i, 52, 84; 1902, i, 537.
i, 756), the author has made a more extended investigation of
them. Oxidation of the corresponding thiocarbamyl compounds by
means of bromine or permanganate affords a convenient general
method for the synthesis of these acids (compare Holmberg, A.,
1905, i, 324; 1907, i, 384; 1910, i, 834; 1912. i, 131), and the
author has studied the methods of preparing the thiocarbamyl-
glycollic acids necessary for this synthesis.

Acetaminocarbothiolonglycollic [*monoamide* of *xanthodiacetic*]

acid, $CO_2H \cdot CH_2 \cdot O \cdot CS \cdot S \cdot CH_2 \cdot CO \cdot NH_2$, prepared as sodium salt according to the scheme $CO_2Na \cdot CH_2 \cdot OH + CS_2 + KOH = H_2O +$ $CO_2Na \cdot CH_2 \cdot O \cdot CS \cdot SK$, and this

$+ CH_2Cl \cdot CO \cdot NH_2 \rightarrow CO_2Na \cdot CH_2 \cdot O \cdot CS \cdot S \cdot CH_2 \cdot CO \cdot NH_2$, crystallises in faint yellow prisms and sinters at 123°, m. p. (not sharp) 129—130°.

Trithiocarbodiglycollamide, $CS(S \cdot CH_2 \cdot CO \cdot NH_2)_2$, formed during the above synthesis by the action of chloroacetamide on trithiocarbonate derived from the carbon disulphide and alkali, crystallises in golden spangles, m. p. 206—207° (decomp.) or 198° (slow heating).

Thiocarbamylglycollic acid is formed in best yield from ethyl carbothiolonglycollic acid (compare Holmberg, A., 1907, i, 384), but is more readily obtained pure, as ammonium salt, by the action of ammonia (3 mols.) on the monoamide of xanthodiacetic acid (1 mol.). The ammonium salt forms white needles, m. p. about 160° (decomp.). The free acid shows m. p. 125°, or, with rapid heating, 134—135°, the varying values being caused by conversion of the acid to a greater or less extent into the anhydride; the temperature, 111—112°, given by Holmberg as the melting point of the acid is really that of the anhydride (see below). The ammonium salt formed in the above way is accompanied by dithioglycollamide, $S_2(CH_2 \cdot CO \cdot NH_2)_2$, m. p. 157·5—158·5° (Claësson, A., 1881, 580, gave m. p. 155°), which results from the oxidation in the air of thioglycollamide (compare Klason and Carlson, A., 1906, i, 232), this being also a product of the decomposition of the monoamide of xanthodiacetic acid by ammonia.

The action of ammonia on carbothiolondiglycollic acid yields, besides the ammonium salt of thiocarbamylglycollic acid, also that of trithiocarbodiglycollic acid, $CS(\cdot S \cdot CH_2 \cdot CO_2H)_2$, m. p. 172—173° (compare Holmberg, A., 1905, i, 324).

Thiocarbamylglycollic anhydride [4 - keto - 2 - thionoxazolidine]

$O < \begin{smallmatrix} CH_2 \cdot CO \\ CS—NH \end{smallmatrix} >$, forms a woolly mass of soft, hair-like crystals, m. p. 111—112°, and is not converted into the corresponding acid on dissolution in water. The compound, m. p. 143°, obtained by heating thiocarbamylglycollic acid with acetic anhydride, and described by Holmberg (A., 1909, i, 286; 1912, i, 130) as this anhydride, consists of carbamylglycollic acid. In virtue of its iminic hydrogen, the anhydride exhibits acid characters, and may be determined titrimetrically.

Ethylthiocarbamylglycollic anhydride [4-keto-2-thion-3-ethyl-oxazolidine] (compare Holmberg, A., 1912, i, 131), prepared by the action of ethylamine on either carbothiolondiglycollic acid or the monoamide of xanthodiacetic acid, forms crystals, m. p. 40—41°, and is accompanied by thioglycollic acid, b. p. 107—108°/16 mm. When converted by alkali into a salt of the corresponding acid and oxidised by means of bromine, it yields ethylcarbamylglycollic acid, m. p. 87—88°.

Diethylthiocarbamylglycollic acid, crystals, m. p. 90·5—91°, i.

btained by the action of diethylamine on either ethylcarbothiolon-lycollic acid or carbothiolonglycollic acid or its mono-amide; the roduct obtained from the last two acids crystallises well and is ccompanied by thioglycollic acid.

In preparing carbamylglycollic acids from the corresponding hiocarbamylglycollic acids, the best oxidising agent is bromine, the ction of permanganate resulting in poor yields and often in impure roducts.

Carbamylglycollic acid thus obtained melts at temperatures vary-1g from 155° to 161°, according to the rapidity of heating, the cid undergoing more profound change than mere conversion into nhydride. The potassium, barium ($+H_2O$), and silver salts, and 1e ethyl ester, m. p. 64—65° (Thiele and Dent, *loc. cit.*, give 61°), ere prepared. When heated in aqueous solution, the acid decom-oses into glycollic acid, carbon dioxide, and ammonia.

Carbamylglycollic anhydride (2:4-diketo-oxazolidine),

$$O \Big\langle \begin{matrix} CH_2 \cdot CO \\ CO-NH' \end{matrix}$$
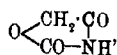
. p. 89—90°, cannot be obtained by heating the corresponding iid, but may be prepared by oxidation of thiocarbamylglycollic nhydride by means of bromine (compare Traube and Ascher, A.,)13, i, 901). It exhibits acid properties, and when titrated with rium hydroxide solution gives a sharp colour change with phenol-hthalein. When heated in aqueous solution or in presence of iid, the anhydride undergoes no appreciable decomposition, and ie ammonia evolved on distillation with concentrated alkali hydr-tide is less than the calculated quantity.

Ethylcarbamylglycollic acid, prepared from ethylthiocarbamyl-ycollic anhydride by the action of bromine or permanganate in tassium hydroxide solution, has m. p. 87—88° (Holmberg, A.,)12, i, 131, gave 85—86°). The potassium, barium ($+H_2O$), and ver salts, the *ethyl* ester. $CO_2Et \cdot CH_2 \cdot O \cdot CO \cdot NHEt$, m. p. 46—47°, id the *amide*, $C_5H_{10}O_2N_2$, m. p. 120·5—121·5°, were prepared. hen heated in aqueous solution or in presence of acid, the acid composes, with formation of glycollic acid, carbon dioxide, and hylamine; with concentrated alkali hydroxide, the decomposition quantitative.

Ethylcarbamylglycollic anhydride [2:4-diketo-3-ethyloxazolidine], $\Big\langle \begin{matrix} CH_2 \cdot CO \\ CO-NEt' \end{matrix}$ forms a colourless oil with a characteristic odour, p. 119·5°/12 mm., D_4^{20} 1·246, n_D^{15} 1·462. By cold barium hydr-de solution, it is decomposed, apparently, into glycollethylamide, HEt·CO·CH₂·OH, but when heated in aqueous or acid solution remains almost entirely undecomposed. The methylene group of anhydride does not react with benzaldehyde in presence of acetic ivdride in the same way as that of ethyl- and phenyl-thiocarb-ylglycollic anhydrides (compare Holmberg. A., 1912, i, 133), the separable product of the reaction being benzvlidene acetate.
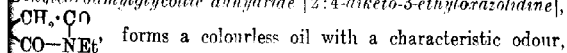
Diethylcarbamylglycollic acid, $CO_2H \cdot CH_2 \cdot O \cdot CO \cdot NEt_2$, prepared

by the action of either bromine in alkaline solution or permanganate on diethylthiocarbamylglycollic acid, forms colourless needles, m. p. 77·5—79°; the *potassium*, *barium*, and *silver* salts are described. The *ethyl* ester, $C_9H_{17}O_4N$, is a mobile liquid with a characteristic fruity odour, b. p. 122—123°/10 mm., D_4^{20} 1·059 n_D^{17} 1·433. Attempts to prepare the amide of the acid resulted in the formation of an uncrystallisable, viscous product, which was not analysed. When heated in aqueous solution or in neutral, acid, or alkaline solution, the acid decomposes into glycollic acid, carbon dioxide, and amine.   T. H. P.

Electrolytic Reaction of Organic Sulphur Compounds. I. Thioamide Group. MOTOOKI MATSUI and EITARO ASHIDA (*J. Tokyo Chem. Soc.*, 1919, **40**, 147—156).—A compound like carbamide, containing the carbamyl group, is known to react as an imino-compound. According to Werner, the iminocarbamic acid formula expresses the true nature of carbamide. Matsui previously showed (*ibid.*, **30**, 1157) that thioamide groups must be represented by the imino-formula, RC(:NH)·SH. As a further proof for this contention, he and Ashida argue that if the thioamide group acts as an imino-acid, then electrolytic oxidation ought to produce a double sulphur compound, containing two groups of $>$C(:NH) and –SC(:NH)–. Experimental results seem to confirm their hypothesis. To 1·32 grams of thiocarbamide in 106 c.c. of alcohol are added 4 c.c. of nitric acid (D 1·22). After passing a current of 0·3 to 0·4 ampere for five hours, there appears at the positive platinum pole a white, needle-shaped compound, yielding 1·06 grams after repeated purifications. Analysis shows it to be dithioform-amidine dinitrate, [SC(:NH)·NH₂]₂,2HNO₃. From acetylthiocarb-amide they obtained dithiomonoacetylformamidine. From mono-phenylthiocarbamide, H₂N·C(:NPh)·S·S·C(:NH)·NH₂, is obtained. Thiobenzamide in alcohol is known to be oxidised by iodine to 3:5-diphenyl-1:2:4-thiodiazole. By electrolytic oxidation, they obtained the identical compound, namely, $S\begin{smallmatrix}N=CPh\\CPh:N\end{smallmatrix}$, m. p. 90°, instead of the dithio-compound. In the same way, thioacetanilide yields $C_6H_4\begin{smallmatrix}S\\N\end{smallmatrix}>CMe$. Although, thus, they failed to obtain dithio-compounds in the last two cases, still they believe that the reactions in every case could be explained only on the assumption that the thioamide group has the structure RC(:NH)·SH.

CHEMICAL ABSTRACTS.

The Catalytic Reduction of Hydrogen Cyanide. SYDNEY BARRATT and ALAN FRANCIS TITLEY (T., 1919, **115**, 902—907).

New Method of Preparation of some Polynitro-aromatic Compounds. MARQUEYROL and LORIETTE (*Bull. Soc. chim.*, 1919, [iv], **25**, 370—375).—For the preparation of compounds of the type

of trinitrophenol, the authors recommend that the nitration should be carried out in three stages. The phenol ($\frac{1}{2}$ mol.) is converted into p-phenolsulphonic acid, which is then diluted with water and poured into a cold aqueous solution of sodium nitrate, the product being sodium 2-nitrophenol-4-sulphonate. To this solution, nitric acid ($\frac{1}{2}$ mol.) is then added, a mixture of 2:4-dinitrophenol and sodium 2:6-dinitrophenol-4-sulphonate being obtained. After cooling, the dinitrophenol is separated by filtration, and may be further nitrated, and to the filtrate more nitric acid ($\frac{1}{2}$ or 1 mol.) is added, and the liquid brought to the boil. By this means, very pure picric acid is obtained with a good yield. This procedure is of advantage in that practically no nitrous fumes are liberated, and but little more than the theoretical quantities of sulphuric and nitric acids are required.

This method may be applied to commercial cresol. In the first stage, any o-cresol present yields o-cresol-5-sulphonic acid, the m-cresol gives m-cresol-6-sulphonic acid, and the p-cresol gives p-cresol-3-sulphonic acid. In the next stage, from these sulphonic acids are formed, respectively, the 3-nitro-derivative, a mixture of the 2-nitro- and 4-nitro-compounds, and the 5-nitro-derivative. In the third stage, the o- and p-cresols will yield simply their 3:5-dinitro-derivatives, which are insoluble in water, and may be filtered off, whilst from the m-cresol there is obtained sodium 2:4-dinitro-m-cresol-6-sulphonate, which is soluble. The latter compound, when boiled with nitric acid, gives trinitro-m-cresol.

It is suggested that the nitrosulphonic acids of the three cresols may be separated through their potassium salts, since that from p-cresol is only sparingly soluble in water and is formed in the cold; that from o-cresol is only sparingly soluble, and is not formed in the cold, but only at 50°; whilst that from m-cresol is soluble in water and is only formed at 60°. W. G.

Preparation of 2:4-Dinitrophenol by Direct Nitration of Phenol. MARQUEYROL and LORIETTE (*Bull. Soc. chim.*, 1919, [iv], 25, 375).—If phenol is liquefied by the addition of 30 grams of water to 94 grams of the phenol, and this liquid is slowly added to a mixture of 400 c.c. of sulphuric acid (D 1·58) and 270 c.c. of nitric acid (D 1·33), kept well stirred, and cooled until the whole of the phenol is added, the temperature then being allowed to rise to 100°, a yield of 71% of 2:4-dinitrophenol is obtained. W. G.

Oxidation of Phenols. III. Polymerisation of Methylenequinones to Cyclic Dehydrophenols. RUDOLF PUMMERER and EMIL CHERBULIEZ (*Ber.*, 1919, 52, [B], 1392--1402).—Dehydro-1-methyl-β-naphthol is decomposed when heated in xylene solution into 1-methyl-β-naphthol and naphthamethylenequinone, which could not be obtained in the unimolecular state (A., 1915, i, 419); this substance has now been obtained in the form of sulphur-yellow crystals, m. p. 143° (corr.), and is shown to be formed by the condensation of two molecules of the methylenequinone. It appears

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to be dehydro-*αβ*-dinaphthol-2-ethane (annexed formula), since it yields a *monophenylhydrazone*, shining platelets, m. p. 233° (corr.), and is reduced by zinc dust and acetic acid to *αβ-dinaphthol-2-ethane*, m. p. 253° (corr.) (*diacetyl* derivative, monoclinic plates, m. p. 233—234° [corr.]), which is readily reconverted into dehvdrodinaphtholethane by oxidation with potassium ferricyanide in dilute alkaline solution.
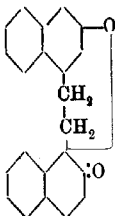
Dehydro-6-bromo-1-methyl-*β*-naphthol (*loc. cit.*) is similarly decomposed by boiling xylene, yielding bromomethylnaphthol and *dehydrodibromodi-naphtholethane*, yellow prisms, m. p. 177° (corr.). The latter gives a *monophenylhydrazone*, small, reddish-brown needles, m. p. 237—238° (corr.), and is reduced to 6 : 6'-*dibromo-αβ-dinaphthol-2-ethane*, needles, m. p. 275° (corr.), which is readily re-oxidised to the parent substance.

Zincke's tetrachloro-*p*-methylenebenzoquinone (A., 1903, i, 757) has been shown to be dehydrotetrachloro-*p*-cresol (*loc. cit.*) from a study of its power to oxidise quinol; this conclusion is now confirmed by observations of its oxidising action on potassium iodide. Determinations of molecular weight in benzene show an almost complete dissociation of the double molecule either into the radicles, or, more probably, into the methylenequinone and tetrachloro-*p*-cresol.

The authors' investigations lead them to consider that the true methylenequinones with an unsubstituted methylene group are exceedingly active substances which readily polymerise. They are therefore of the opinion that the seven compounds described as such in the literature are either quinol ethers or dehydro-substances, and that a methylenequinone with unsubstituted methylene group has not up to the present been isolated in the unimolecular condition.

H. W.

Oxidation of Phenols.   IV.   Constitution of the Dehydro-naphthols and Preparation of Dehydro-α-bromo-β-naphthol. RUDOLF PUMMERER (*Ber.*, 1919, 52, [*B*], 1403—1413).—The three following formulæ are possible for dehydro-1-methyl-*β*-naphthol (compare A., 1915, i, 418):

(I.)   (II.)   (III.)
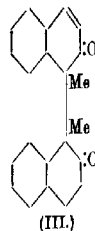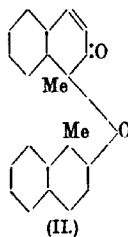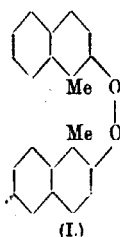
The first explains the ready union of the substance with tri-

phenylmethyl, but is improbable by reason of the yellow colour of the substance and its instability towards permanganate in acetone solution at −40°. The decision between II and III cannot be made with phenylhydrazine, which behaves as a reducing agent. The author has therefore prepared an α-halogen-substituted dehydro-β-naphthol in which, according to II, two halogen atoms must be loosely combined, whilst, according to III, only one is in loose combination. *Dehydro-α-bromo-β-naphthol*, m. p. 115—116°, is prepared by the action of tetrachlorodehydro-*p*-cresol on 1-bromo-β-naphthol; it contains only one reactive bromine atom, since it is hydrolysed in aqueous-alcoholic solution to β-naphthaquinone and 1-bromo-β-naphthol, and is reduced by stannous chloride probably to *a'-bromo-β-hydroxy-αβ'-dinaphthyl ether*, m. p. 135·5—136·5° (corr.), in which the α-position adjacent to the hydroxyl group must be occupied, since it does not yield an azo-dye with benzene-diazonium chloride. The dibromo-compound must therefore have a constitution analogous to that expressed by formula II.

β-Hydroxy-αβ'-dinaphthyl ether is obtained, amongst other products, by the dehydrogenation of β-naphthol by potassium ferricyanide in alkaline solution (compare following abstract); the first product is probably dehydro-β-naphthol, the keto-form of which is not stable and passes into the corresponding enolic form.

The constitution of dehydro-oxydinaphthalene oxide (Pummerer and Frankfurter, A., 1914, i, 714) is further discussed. It readily decolorises potassium permanganate, and hence cannot be an aromatic peroxide; the diketo-formula is also impossible, for reasons previously given, so that there remains only the annexed formula.
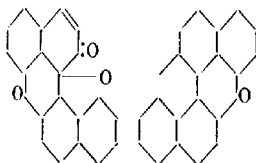
When treated with benzoyl peroxide (subsequent abstract), it absorbs two atoms of oxygen, yielding a compound which is termed a β-peroxide (IV), to distinguish it from the α-peroxide (V) obtained with oxygen. The β-derivative is sharply distinguished from the α-compound by its stability towards permanganate in pyridine solution and by the lemon-yellow colour

(IV.)   (V.)
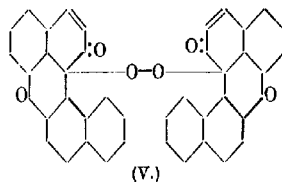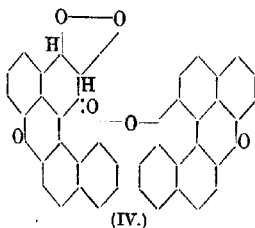
common to all *O*-derivatives of hydroxydinaphthalene oxide, whereas the *C*-derivative (α-peroxide) is pale brown. The β-per-

oxide can only be obtained from the solid dehydro-substance; solutions of the latter, even when concentrated, are rapidly decolorised by benzoyl peroxide without separation of the β-peroxide, whilst the α-peroxide is contained among the products, its formation being primarily due to the dissociation of the dehydro-substance into its component radicles (Pummerer and Frankfurter, *loc. cit.*); the possible tautomerism of the latter is again discussed, and the hypothesis advanced previously (*loc. cit.*) satisfactorily explains the more recent phenomena.   H. W.

Oxidation of Phenols.   V.   Formation of β-Hydroxy-αβ'-dinaphthyl Ether by the Dehydrogenation of β-Naphthol. RUDOLF PUMMERER and EMIL CHERBULIEZ (*Ber.*, 1919, **52**, [*B*], 1414—1415. Compare preceding abstract).—Oxidation of a solution of β-naphthol in the requisite quantity of aqueous sodium hydroxide solution by means of aqueous potassium ferricyanide leads to a mixture of products from which β-hydroxy-αβ'-dinaphthyl ether, colourless needles, m. p. 196°, can be isolated in small amount.   H. W.

Oxidation of Phenols.   VI.   Dehydro-oxydinaphthalene Oxide and Colorimetric Observations of its Dissociation into Radicles. RUDOLF PUMMERER and FRITZ FRANKFURTER (*Ber.*, 1919, **52**, [*B*], 1416—1420. Compare preceding abstracts).—The β-*peroxide* of dehydro-oxydinaphthalene oxide is prepared by the action of a concentrated solution of benzoyl peroxide in benzene on dehydro-oxydinaphthalene oxide at the ordinary temperature; it forms lemon-yellow, microscopic prisms, m. p. 210° (corr.; decomp.), which are reduced by zinc dust and acetic acid to hydroxydi-naphthalene oxide; the latter is also obtained by reduction of the α-peroxide.

The dilutions at which dehydro-oxydinaphthalene oxide is completely dissociated into its radicles have been colorimetrically estimated for a number of solvents (chloroform, benzene, xylene, ethyl ether, ethyl acetate, carbon disulphide, nitrobenzene); the dielectric constant of the solvent appears to have little influence on its dissociating power.   H. W.

Compounds of Arsenic Acid and Catechol. R. F. WEINLAND and JOSEF HEINZLER (*Ber.*, 1919, **52**, [*B*], 1316—1329).—*Catechol semiarsenate,* $AsO(O \cdot C_6H_4 \cdot OH)_3, 4H_2O$, m. p. about 103° after softening at 60°, is readily obtained in large, colourless crystals when concentrated aqueous solutions of arsenic acid and catechol in molecular proportions varying from 1 : ½ to 1 : 3 are mixed. It is slowly hydrolysed in dilute aqueous solutions, more readily in the presence of acids, and is not decomposed by short heating with alkalis. It is stable in diffused light, but darkens on exposure to direct sunlight. It forms beautifully crystalline salts, in which it appears to function as a monobasic acid as far as the experimental evidence at present shows. When titrated with alkali in the

presence of phenolphthalein, the colour change occurs after addition of exactly one equivalent of base, with methyl-orange at a slightly earlier stage; the acid thus appears to be weaker than arsenic acid. The salts are generally prepared by the addition of the base or of a suitable salt of the metal to a concentrated aqueous solution of the acid. The following salts are described: *ammonium* salt, $\left[\mathrm{AsO(O \cdot C_6H_4 \cdot O)_3}\right]\mathrm{{NH_4 \atop H_2}_4}$, plates; *potassium* salt, plates or rods; *sodium* salt $(2\mathrm{H_2O})$, rods, anhydrous, prisms; *silver* salt, minute crystals, very sparingly soluble in water and not sensitive to light; *magnesium* salt $(8\mathrm{H_2O})$; *calcium* salt $(8\mathrm{H_2O})$; *barium* salt $(8\mathrm{H_2O})$; *zinc* salt $(8\mathrm{H_2O})$; *ferrous* salt $(8\mathrm{H_2O})$; *nickel* salt $(8\mathrm{H_2O})$; *cobalt* salt $(8\mathrm{H_2O})$. With the exception of the barium compound, the salts generally crystallise in cubes. The estimation of water of crystallisation is rendered a little uncertain by the difficulty of drying the substances without decomposition.

If a considerable excess of catechol is used in the preparation of the ammonium or potassium salts, *compounds* of the formula $3[\mathrm{AsO(O \cdot C_6H_4 \cdot O)_3}]\mathrm{K(NH_4)H_2, C_6H_4(OH)_2}$ are obtained; catechol is liberated when they are dissolved in hot water, and primary catechol arsenates are formed.

Another *ammonium* salt, which appears to have the composition $3[\mathrm{AsO(O \cdot C_6H_4 \cdot O)_3}]\mathrm{H_3, 7NH_3}$, is also described, but the exact analysis is difficult, as it loses ammonia at the ordinary temperature.

H. W.

The Reduction of *allo*Cinnamic Acid and Coumarin.

YASUHIKO ASAHINA and ATSUSHI FUJITA (*J. Pharm. Soc. Japan*, 1919, No. 444, 97—109).—By reduction of methyl *allo*cinnamate with sodium amalgam, phenylpropionic acid (43%), $\beta\gamma$-diphenyladipic acid, m. p. 175° (6%), and the corresponding *iso*-acid, m. p. 75° (3%), were obtained as their methyl esters. Henle (A., 1906, i, 669), using aluminium amalgam, obtained 55%, 8—9%, and 4—5%, respectively, of the same compounds by reduction of methyl cinnamate. This shows that *allo*cinnamic and cinnamic acids yield essentially the same reduction products. Sodium amalgam is a better reducing agent than aluminium amalgam, since it reacts more rapidly, and the precipitation of aluminium hydroxide is avoided. Coumarin, as a derivative of *allo*cinnamic acid, yields bimolecular reduction products. Dyson (T., 1887, **51**, 68) obtained from salicylaldehyde and sodium succinate a dicoumarin,

$$\mathrm{{C_6H_4 \cdot CH \atop O\!-\!\!-\!\!-CO}}\!\!>\!\!\mathrm{C \cdot C}\!\!<\!\!\mathrm{{CH \cdot C_6H_4 \atop CO\!-\!O}},$$
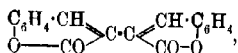
which he reduced to dihydrocoumaric acid,

$$[\mathrm{CH(CO_2H) \cdot CH_2 \cdot C_6H_4 \cdot OH}]_2.$$
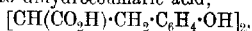
and to dihydrocoumarin, m. p. 222—224°. Fries and Fickewirth (A., 1908, i, 822) obtained, by reduction of coumarin and dehydration of the resulting tetrahydrodicoumaric acids, two tetrahydrodicoumarins, m. p. 284° and 256° respectively. The former they

designated α, the latter β, and to the acids they assigned the Dyson dihydrocoumaric acid formula shown above. This formulation is incorrect; two coumarin nuclei must necessarily unite in the β-position, whereas Dyson's dihydrocoumarin is linked in the α-position. Its reduction products are derivatives of succinic acid, whilst the products of direct reduction of coumarin are βγ-disubstituted adipic acids. This was established experimentally by repeating Fries and Fickewirth's preparation of the tetrahydrocoumarins, which were obtained with m. p. 284° and 256°, just as described by those authors, and comparing them with reduction products of dicoumarin prepared as described by Dyson. The latter process yielded two dihydrocoumarins, m. p. 243° and 248° respectively, but when mixed they had m. p. 222—224°. It was evidently this mixture which Dyson obtained. Neither is identical with either of the tetrahydrocoumarins of Fries and Fickewirth. It is therefore proposed to call Dyson's compound α-dicoumarin, and the two derivatives (of which he had the mixture) α- and β-tetrahydro-α-dicoumarin. The tetrahydro-derivatives of Fries and Fickewirth are, then, to be considered as derivatives of an unknown β-dicoumarin.   CHEMICAL ABSTRACTS.

The Acylsemicarbazides and the Acylhydroxamides (**Rectification**). J. BOUGAULT (*Bull. Soc. chim.*, 1919, [iv], 25, 384—386).—As a result of further analyses, the author now finds that the compounds obtained by the action of iodine and sodium carbonate on the semicarbazones and oximes of α-ketonic acids, and previously described as acylsemicarbazides and acylhydroxamides (compare A., 1916, i, 764, 765; 1917, i, 417, 688, 694), do not possess the constitution then assigned to them. Instead of a molecular composition, $R \cdot CO \cdot NH \cdot NH \cdot CO \cdot NH_2$, as given to the acylsemicarbazides, the elements of a molecule of water should be deducted, giving an empirical formula $R \cdot C_2H_3ON_3$, the constitution of which has not been elucidated. Similarly, where the acylhydroxamides were assigned the constitution $R \cdot CO \cdot NH \cdot OH$, the formula should now be written $R \cdot CON$, and their constitution is considered to be

either $\begin{matrix} CPh\text{-}CPh \\ || \quad || \\ NO \cdot ON \end{matrix}$ or $\begin{matrix} CPh \cdot CPh \\ || \quad | \\ N \cdot O \cdot N \end{matrix} > O$. It has been shown that the

so-called acylhydroxamide obtained from phenylglyoxylic acid is identical with diphenylglyoxime peroxide.   W. G.

Truxillic Acids and Truxones. R. STOERMER and G. FOERSTER (*Ber.*, 1919, **52**, [*B*], 1255—1272).—The recent publication of Stobbe (this vol., i, 329) has induced the authors to describe a series of experiments which are still partly unfinished.

*allo*Cinnamic acid is transformed by the light of a quartz lamp into β-*iso*truxillic acid; in sunlight, the same acid is also formed, occasionally accompanied by α-truxillic acid. Depolymerisation of β-*iso*truxillic and α-truxillic acids occurs when solutions of their sodium salts are exposed to the light of a quartz lamp, *trans-* and *allo*-cinnamic acids being formed from the former acid, cinnamic

and, possibly, *allo*cinnamic and γ-truxillic acids from the latter
acid. Attempts to polymerise crotonic, fumaric, β-phenylcinnamic,
and *cis*- or *trans-p*-methoxycinnamic acids by sunlight were un-
successful; β-methylcinnamic acid, however, gave dimethyltruxillic
acid, m. p. 217—218°.

α-Truxone, m. p. 293°, is conveniently prepared by the action of
aluminium chloride on a solution of α-truxillyl chloride in carbon
disulphide; the dioxime, m. p. above 300°, is converted by methyl
sulphate into the *dimethyl ether*, m. p. 214°. The molecular weight
of the latter has been determined in benzene solution, and the
results confirm the formula, $(C_9H_6O)_2$, for truxone. γ-Truxillic
acid could not be converted into a truxone by sulphuric acid, but
yielded α-truxone with aluminium chloride; β- and δ-*iso*truxillic
acids were either unchanged or merely sulphonated by sulphuric
acid.   ✦

α- and γ-*Diphenyltruxones* are prepared by the action of fuming
sulphuric acid on β-phenylcinnamic acid or β-hydroxy-β-phenyl-
hydrocinnamic acid, and are separated by fractional crystallisation
from acetone or from a mixture of alcohol and acetic acid; the
former crystallises in rods or plates, m. p. 253°, whilst the latter
has m. p. 224°, and is converted when heated at about 225° into
the α-derivative. The following derivatives are described:
α-*diphenyltruxone monoxime*, six-sided crystals, m. p. 273·5°
(*methyl ether*, colourless needles, m. p. 208°); α-*diphenyltruxone
dioxime*, needles, m. p. 262°; γ-*diphenyltruxone monoxime*, needles,
m. p. 235° (*methyl ether*, m. p. 170°); γ-diphenyltruxone dioxime,
m. p. 270·5—271°. The hydroxylamino-group is readily removed
by treatment of the oximes with alcohol at 100°, the corresponding
truxones being regenerated. α-*Diphenyltruxone monophenylhydr-
azone* forms yellow crystals, m. p. 153—154°, whilst the monophenyl-
hydrazone of the γ-compound has m. p. 128—129°. Attempts to
reduce the truxones completely by Clemmensen's method, by sodium
amalgam, zinc and acetic acid, or zinc and potassium hydroxide
were unsuccessful, the process coming to an end with the produc-
tion of the diol. In these circumstances, γ-diphenyltruxone yields
α-*diphenyltruxandiol*; isomerisation is not induced by hydrochloric
acid or potassium hydroxide alone, so that the nascent hydrogen
appears to have an isomerising as well as a reducing action.
α-Diphenyltruxandiol has m. p. 234·5°; the *monoacetate* (possibly
not quite pure) melts at 235—237°, the *diacetate* at 215—216°.
The α- and γ-*diphenyltruxanes* were, however, prepared from the
corresponding truxones by the action of hydrazine and sodium
ethoxide; the former has m. p. 201—202°. γ-*Diphenyltruxone
dihydrazone* forms small crystals, m. p. 254°, and is converted by
sodium ethoxide into a mixture of α-diphenyltruxane and
γ-diphenyltruxane, m. p. about 169—171°, but the latter could
not be prepared in the pure condition on account of lack of
material. The latter is completely converted into the α-isomeride
when heated for five hours at a temperature slightly above its melt-
ing point.   H. W.

Constitution of Bile Acids. II. Dehydrocholanic Acid. W. BORSCHE (*Ber.*, 1919, **52**, [*B*], 1353—1365. Compare Borsche and Rosenkranz, this vol., i, 276).—Further experiments with dehydrocholanic acid lead the author to adopt Schenk's view of its constitution, and thus to consider it as a triketocarboxylic acid containing the ·CO·CH₃ group; all attempts to identify the presence of an aldehydic group were unsuccessful, whilst it has been found possible to condense the substance with aromatic aldehydes, thus obtaining conclusive evidence of the presence of the ·CO·CH₃ group. One of the carbonyl groups of dehydrocholanic acid is more reactive than the remaining two, and thus gives rise to acetals when the acid is esterified, whilst also it is the first to suffer reduction; the compound thus formed, which was previously described as deoxy-dehydrocholanic acid, is now designated β-dehydrodeoxycholanic acid, to avoid confusion with the primary product of the oxidation of deoxycholanic acid.

Methyl dehydrocholanate, $C_{25}H_{36}O_5$, is prepared by the esterification of dehydrocholanic acid in the presence of a considerable amount of hydrogen chloride or sulphuric acid; it crystallises in silky needles, m. p. 241—242°, which are very sparingly soluble in methyl alcohol. It forms a *trioxime*, leaflets, m. p. 265—266°, and a *triacetyl* derivative, which gradually melts from about 60°. *Methyl dehydrocholanate dimethylacetal*, $C_{27}H_{42}O_6$, is formed by treating the ester or the acid with methyl alcohol containing 1% of hydrogen chloride or 3% of sulphuric acid; it forms long needles, m. p. 140°, and is freely soluble in warm methyl alcohol. It is reconverted into the ester by concentrated methyl-alcoholic solutions of mineral acids, and is hydrolysed to dehydrocholanic acid by alkali. With hydroxylamine, it gives the trioxime of methyl dehydrocholanate. The acetal nature of the substance is proved by the fact that methyl alcohol is readily eliminated when it is heated, and that it yields an *enol ether*, $C_{26}H_{38}O_5$, colourless leaflets, m. p. 173—174°, b. p. 333—334°/16 mm. Methyl-alcoholic potassium hydroxide solution converts it into dehydrocholanic acid, whilst hydroxylamine transforms it into the trioxime of methyl dehydrocholanate. It readily absorbs bromine, but methyl bromide appears to be eliminated simultaneously. A similar substance. m. p. 170—172° (decomp.), appears to be formed by the action of a 2% solution of sulphuric acid in ethyl alcohol on dehydrocholanic acid, but the product is readily converted into ethyl dehydrocholanate, m. p. 221°.

β-Deoxydehydrocholanic acid, needles, m. p 176°, is prepared mixed with unchanged acid, and cholanecarboxylic acid by the reduction of dehydrocholanic acid by amalgamated zinc and hydrochloric acid; it crystallises also with $1H_2O$, m. p. 115°. The ethyl ester crystallises in colourless needles. m. p. 152—153°, and yields a *dioxime*, pearly leaflets, m. p. 242° (decomp.).

Cholanecarboxylic acid, m. p. 160°, is obtained in 55—60% yield by the reduction of dehydrocholanic acid by Clemmensen's method. The following derivatives have been prepared: *ethyl* ester, colour-

less, coarse needles, m. p. 92°; *chloride*, m. p. 128°; *amide*, minute, hexagonal prisms, m. p. 75°. H. W.

Preparation and Uses of Semi-oxamazide. L. G. RADCLIFFE (*Perfumery and Essen. Oil Rec.*, 1919, **10**, 39—42).—During a study on certain aromatic aldehydes, it became necessary to prepare their semi-oxamazones, and preliminary thereto the requisite semi-oxamazide. Detailed descriptions are accordingly given for the preparation of ethyl oxalate, oxamethane, and the finished reagent. Many of the semi-oxamazones described had been previously prepared by Kerp and Unger (A., 1897, i, 269), and include those of benzaldehyde, *p*-toluic, *p-iso*propylbenzoic, anisic, cinnamic, salicylic and phenylacetic aldehydes, vanillin, piperonal, citral and furfuraldehyde, acetophenone, phenyl ethyl ketone, styryl methyl ketone, benzophenone, and menthone. CHEMICAL ABSTRACTS.

A New Method of Obtaining Bicyclic Ketones. FÉLIX TABOURY and MARCEL GODCHOT (*Compt. rend.*, 1919, **169**, 62—64). —*cyclo*Pentanone and *cyclo*hexanone and their homologues are readily converted into unsaturated bicyclic ketones when their vapours are passed over calcium hydride. Calcium carbide is not so satisfactory a condensing agent, only giving a good result with *cyclo*pentanone out of the four ketones examined. W. G.

Synthesis of Ketimines by Catalytic Methods. GEORGES MIGNONAC (*Compt. rend.*, 1919, **169**, 237—239).—It has been found possible to prepare certain ketimines by passing the vapour of the ketone, along with ammonia, over thorium oxide at 300—400°, the temperature varying with the ketone used. This method is not applicable to purely aliphatic ketones, owing to the readiness with which their ketimines undergo condensation. Successful results were obtained with acetophenone, propiono-phenone, and benzophenone, but only a very small yield was obtained from *cyclo*hexanone.· W. G.

Hydrogenation of Piperonal Ketone and of Dipiperonal Ketone. VAVON and FAILLEBIN (*Compt. rend.*, 1919, **169**, 65—67). —The method with platinum black previously described (compare A., 1914, i, 694) may be used satisfactorily for the hydrogenation of piperonal and dipiperonal ketones. In the latter case, the reaction takes place in two stages, giving first *dihydropiperonal ketone*,

$$CH_2\!\!<^O_O\!\!>\!\!C_6H_3\cdot CH\!:\!CH\cdot CO\cdot CH_2\cdot CH_2\cdot C_6H_3\!\!<^O_O\!\!>\!\!CH_2, \quad m. p. 99°,$$

and then the fully saturated *ketone*, $CO(CH_2\cdot CH_2\cdot C_6H_3\!\!<^O_O\!\!>\!\!CH_2)_2$,

m. p. 55°. Both the yellow and the white forms of piperonal ketone, as described by Haber (compare A., 1891, 704), on hydrogenation give the same saturated *ketone*, m. p. 51°, b. p. 168°/13 mm., giving an *oxime*, m. p. 98°, and a *semicarbazone*, m. p. 166°. The authors consider that the yellow form, m. p. 107°,

as described by Haber, is but an impure specimen of the white form, m. p. 111°.
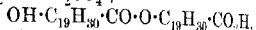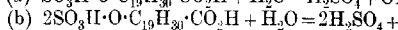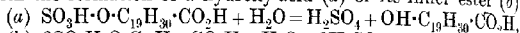
W. G.

Alcoholysis of Balsams. ERNEST FOURNEAU and MARIO CRESPO (*Bull. Soc. chim.*, 1919, [iv], **25**, 386—389).—The process which consists in boiling the balsam for six hours with an equal weight of ethyl alcohol containing 3% of hydrogen chloride, neutralising the product with sodium carbonate, and distilling off the esters and alcohols in steam, does not attack the resins. The esters and alcohols are separated by fractional distillation. The results indicate that the balsams are a mixture of cinnamyl and benzyl cinnamates and benzoates in varying proportions, and resins.

W. G.

The Action of Sulphuric Acid on Colophony. AD. GRÜN (*Chem. Umschau Fett. Ind.*, 1919, **26**, 77—79).—When colophony is mixed with light petroleum and treated with sulphuric acid for several hours at —5°, the sulphuric acid combines with the double bond of the abietic acid,

$$C_{19}H_{29} \cdot CO_2H + H_2SO_4 = SO_3H \cdot O \cdot C_{19}H_{30} \cdot CO_2H,$$
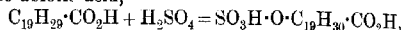
and on boiling the sulphuric acid ester with water, it is decomposed with the formation of a hydroxy-acid (*a*) or its inner ester (*b*):

(*a*) $SO_3H \cdot O \cdot C_{19}H_{30} \cdot CO_2H + H_2O = H_2SO_4 + OH \cdot C_{19}H_{30} \cdot CO_2H,$
(*b*) $2SO_3H \cdot O \cdot C_{19}H_{30} \cdot CO_2H + H_2O = 2H_2SO_4 +$
$$OH \cdot C_{19}H_{30} \cdot CO \cdot O \cdot C_{19}H_{30} \cdot CO_2H,$$

or a mixture of the two products. From the acid value and acetyl value of the product obtained in one experiment, it was calculated that it consisted of 64·1% of the inner ester, 26·5% of unaltered abietic acid, and 9·4% of unsaponifiable matter. Esterification of colophony with sulphuric acid in the presence of methyl alcohol, and decomposition of the product by boiling with water, yields only the methyl ester of abietic acid. with not more than a trace of hydroxy-acid. The methyl ester absorbs only two molecules of halogen when treated with Wijs' iodine chloride solution, whereas the free abietic acid absorbs three molecules. [See also *J. Soc. Chem. Ind.*, 1919, 589A.]

C. A. M.

Researches on Chlorophyll. XXV. Phytol. II. RICHARD WILLSTÄTTER, OTTO SCHUPPLI, and ERWIN W. MAYER (*Annalen*, 1919, **418**, 121—147).—The supposed difference between the oxidation products of crude and distilled phytol (compare Willstätter, Mayer, and Hüni, A., 1911, i, 144) is found to be non-existent. α- and β-phytols containing the double linking in the same position. After distillation. phytol does, however, lose water the more readily, especially when heated with phthalic anhydride or acetic acid, probably owing to the existence of two geometrically isomeric forms of the alcohol. The purest preparations of the ketone, obtained by oxidising phytol, have compositions agreeing well with the formula $C_{15}H_{30}O$, but they all contain oxygen-rich admixtures. which are most persistently retained. Repeated conversion of the ketone into its 1-naphthylhydrazine-4-sulphonic acid derivative, followed by

crystallisation and hydrolysis, yields a purified product, the formula of which is most probably $C_{17}H_{34}O$. The action of ozone or chromic acid on this product gives, not a lower ketone, but simply admixtures of increasing oxygen content. The fatty acid occurring with the ketone, and also formed from the latter on oxidation, has not the formula formerly assumed, namely, $C_{14}H_{28}O_2$, but is most probably $C_{16}H_{32}O_2$. Phytol therefore contains the double linking between the third and fourth carbon atoms, and phytenic acid, which is readily converted into an isomeric lactone, should possess the formula $C_{15}H_{31} \cdot CMe \vdots CMe \cdot CO_2H$, since Fichter, Kiefer, and Bernouilli's results (A., 1910, i, 88) show that alkyl groups in the α- and β-positions produce instability of the Δ^1-acids towards 60% sulphuric acid, being transformed thereby completely into lactones.

The hypothetical structure suggested for phytol by Willstätter, Mayer, and Hüni (loc. cit.) thus becomes improbable, the occurrence of derivatives with branched carbon atom chains and of none with normal chains among the oxidation products indicating complex branching of the carbon atom skeleton of phytol.

The purification or isolation of ketones or aldehydes by converting them into derivatives which contain an acidic group, and hence yield salts capable of crystallisation, is illustrated by various examples.

Thus, methyl-ethyl-ketone-phenylhydrazone-m-carboxylic acid, $C_{11}H_{14}O_2N_2$, obtained by the action of m-hydrazinobenzoic acid on the ketone, crystallises in plates, m. p. 143°. Methyl-hexyl-ketone-phenylhydrazone-m-carboxylic acid does not crystallise, but its ammonium salt, $C_{15}H_{25}O_2N_3$, crystallises in bundles of leaflets, m. p. 151°. Methyl-nonyl-ketone-phenylhydrazone-m-carboxylic acid forms spherical, crystalline aggregates, m. p. 93°, but is unstable; its ammonium salt, $C_{18}H_{31}O_2N_3$, crystallises in colourless leaflets, m. p. 146—147° (frothing). Methyl-stearyl-ketone-phenylhydrazone-m-carboxylic acid, $C_{26}H_{44}O_2N_2$, forms spherical, crystalline nodules, m. p. 83—84° (decomp.), and its ammonium salt, which crystallises in leaflets, m. p. 136° (decomp.), is, like the compounds described above, converted quantitatively into the ketone by boiling 17% sulphuric acid. Carvone-phenylhydrazone-m-carboxylic acid, $C_{17}H_{20}O_2N_2$, separated from commercial carvone mixed with four times its quantity of limonene, forms rhombic plates, m. p. 158°. Methyl-nonyl-ketone-1-naphthylhydrazone-4-sulphonic acid gives a crystalline sodium salt, m. p. 250—252° (decomp.). Methyl-succinic-acid-1-naphthylhydrazone-4-sulphonic acid, obtained by hydrolysing the ketone-1-naphthylhydrazone-4-sulphonic acids by means of methylsuccinic acid, forms a potassium salt,

$$C_{13}H_{11}O_6N_2SK + \tfrac{1}{2}H_2O,$$

which crystallises in yellow leaflets, loses its water of crystallisation at 100—110°, and has m. p. 203—204° (decomp.).

When treated with potassium 1-naphthylhydrazine-4-sulphonate, the ketone obtained by oxidising phytol by means of either ozone or chromic acid gives a potassium salt, $C_{27}H_{41}O_3N_2SK$, which crystallises in slender, white needles sintering at 140°, m. p.

164—165° (decomp.). The ketone yields a semicarbazone, $C_{18}H_{37}ON_3$, m. p. 66·5—67°. The pure *ketone*, $C_{17}H_{34}O$, obtained by hydrolysis of either the above potassium salt or the semicarbazone, contains 3—4% of the enolic modification, and forms a colourless, mobile liquid, b. p. 175—175·5°/11 mm., D_4^0 0·844, D_4^{20} 0·834, n_D^{20} 1·44516. Its *oxime*, $C_{17}H_{35}ON$, is a colourless, viscous oil, b. p. 201·6—202°/9 mm., D_4^0 0·879. The alcohol, $C_{17}H_{36}O$, obtained by reducing the ketone by means of sodium and alcohol, forms a viscous oil, b. p. 176—177·5°/10 mm., D_4^0 0·847, D_4^{20} 0·837, n_D^{20} 1·45037. When heated with phosphoric oxide, this alcohol gives the olefine, $C_{17}H_{34}$, b. p. 288—291°/719 mm., 153—155·5°/10 mm., D_4^{20} 0·790, which in acetic acid solution is converted by platinum and hydrogen into the corresponding paraffin, $C_{17}H_{36}$, b. p. 161—162°/15 mm., D_4^0 0·794, D_4^{26} 0·780, n_D^{20} 1·43763. This paraffin is not identical with the saturated hydrocarbon previously described as a product of the fractional distillation of the crude ketone. The formation of the hydrocarbon, $C_{15}H_{32}$, b. p. 131—132°/13 mm., 249—250°/718 mm., as a by-product of the hydrolysis of phytol ozonide is confirmed.

The action of ozone on the ketone in ethyl chloride solution yields the peroxide, $C_{17}H_{34}O_2$, as an oil, D_4^0 0·899, D_4^{20} 0·885, with a piercing odour. A considerable part of the oxygen taken up is lost when the peroxide is distilled, even under diminished pressure. It gives an intense reddish-brown coloration with titanium sulphate and liberates iodine, but not in the calculated proportion, from acid or neutral potassium iodide solution. Even the most active reducing agents convert the peroxide, not into the original ketone, but into products containing more oxygen than this; from these products or from the peroxide itself, the pure ketone may, however, be obtained by way of the semicarbazide. Similar behaviour is exhibited by *methyl nonyl ketone peroxide*, $C_{11}H_{22}O_2$, which forms a colourless oil of piercing odour.

The oily, fatty acids formed together with formic acid by oxidising phytol in various ways, by oxidising the ketone, $C_{17}H_{34}O$, by means of either chromic acid or alkaline bromine solution, or by boiling the ozonide of the hydrocarbon, $C_{17}H_{34}$, apparently range in formula from $C_{16}H_{32}O_2$ to $C_6H_{12}O_2$. The ozonide yields also a *hydrocarbon*, $C_{14}H_{30}$(?), b. p. 114—117°/11 mm., 241—244°/723 mm., and this, when oxidised, gives a mixture of carboxylic acids and a carbonyl *compound*, (? ketone), $C_{12}H_{24}O$, which is a mobile liquid, b. p. 84°/14 mm., 188—189°/726 mm., with the odour of lemons, and forms a *semicarbazone*, m. p. 121—123°.

Fractionation of the acids formed on degradation of the olefine $C_{17}H_{34}$, and purification by means of the *silver* salt, m. p. 191—193°, gives mainly the acid, $C_{16}H_{32}O_2$, b. p. 201—204°/13 mm., D_4^0 0·901, D_4^{20} 0·887, n_D^{20} 1·44967; the corresponding *amide*, $C_{16}H_{33}ON$, forms leaflets, m. p. 46·5—48·5°.   T. H. P.
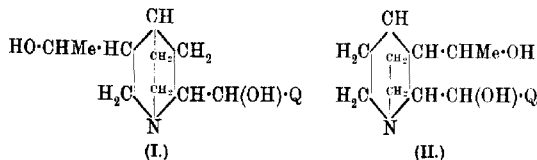
β-Homochelidonine. KANJIRO MOMOYA (*J. Pharm. Soc. Japan*, 1919, No. 444, 110—118 and 6—8).—Protopine and β-homo-

chelidonine, occurring in the alcoholic extract of the roots of *Macleya cordata*, are best separated by means of dilute aqueous ammonia. At 13°, the solubility of protopine in 1% aqueous ammonia is 1·15 grams per litre, whilst that of β-homochelidonine is 6·0 grams per litre. Still further purification is possible through the hydrochlorides; 100 c.c. of water at the ordinary temperature dissolve 14·5 grams of β-homochelidonine hydrochloride, but only 0·7 gram of protopine hydrochloride.

β-Homochelidonine yields two crystalline *compounds* with methyl iodide, one $(1H_2O)$, easily soluble, m. p. 198°, the other $(3H_2O)$, sparingly soluble, m. p. 211°. With methyl sulphate, it yields a *methosulphate* $(3H_2O)$, m. p. 215°. With mercuric acetate, it yields a new base, *dehydro-β-homochelidonine*, which melts at 136°, re-solidifies, and melts again at 203—204°. It is optically inactive, dissolves in ethyl alcohol and in chloroform, but is sparingly soluble in water. By oxidation with potassium permanganate, it yields *m*-hemipinic acid and an acid, $C_{11}H_{11}O_4N$, which was not further studied.   CHEMICAL ABSTRACTS.

Cinchonidine. E. LÉGER (*Compt. rend.*, 1919, **169**, 67—70).— With hydrobromic acid (D 1·5), cinchonidine yields *hydrobromo-cinchonidine hydrobromide*, m. p. 95°. When heated for forty-eight hours with 50% sulphuric acid, cinchonidine gives *hydroxy-dihydrocinchonidine*, $C_{19}H_{24}O_2N_2$, m. p. 242—243° (corr.), $[a]_D - 101·7°$ (in alcohol), giving a *diacetyl* derivative. It is formed by the addition of the elements of water to the grouping CH_2:CH· to give the grouping CH_3·$CH(OH)$·. When heated with 70% sulphuric acid at 115° for ten hours, hydroxydihydrocinchonidine yields *apo*cinchonidine and β-cinchonidine, thus differing from the oxydihydrocinchonines, which give cinchonigine, cinchoniline, and *apo*cinchonine. Based on these observations, the author suggests for hydroxydihydrocinchonidine and α- and β-hydroxydihydro-cinchonines the constitutions indicated in formulæ I and II respectively, where Q represents the quinoline residue:

$$HO·CHMe·HC \underset{H_2C}{\overset{CH}{\diagdown}} \overset{CH_2}{\underset{CH_2}{\diagup}} CH_2$$

$$H_2C \diagup CH·CH(OH)·Q$$

(I.)

$$H_2C \underset{H_2C}{\overset{CH}{\diagdown}} \overset{CH_2}{\underset{CH_2}{\diagup}} CH·CHMe·OH$$
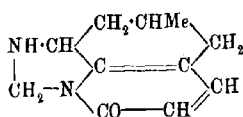
$$CH·CH(OH)·Q$$

(II.)

W. G.

Constitution of Cytisine. ERNST SPÄTH (*Monatsh.*, 1919, **40**, 15—33).—The author discusses previous publications on the constitution of cytisine (Partheil, A., 1893, i. 119; 1894, i, 558; 1895, i, 119, 254; Freund and Friedmann, A., 1901, i, 288; Freund, A., 1904, i, 263; Freund and Horkheimer, A., 1906, i, 302), more particularly those of Ewins (T., 1913, **103**, 97) and Freund and Gauff

(*Arch. Pharm.*, 1918, **256**, 33).   The author shows (following abstract) that the cytisoline obtained by Freund by the action of hydriodic acid and red phosphorus on cytosine is 2-hydroxy-6 : 8-dimethylquinoline.   As regards the presence or absence of the quinoline ring in the cytosine molecule, the assumption that the pyridine or benzene nucleus of cytisoline arises by extension of a five-membered ring is an improbable one; further, van de Moer's reaction (A., 1891, 946; also Gorter, A., 1896, ii, 344) indicates distinctly the presence of an α-pyridone residue in cytisine.   The 6- and 8-methyl groups of cytisoline may exist in the same positions in cytisine, or, as Ewins suggested (*loc. cit.*), that in the 6-position may have arrived by migration during the conversion of cytisine into cytisoline.   The oxygen atom most probably occupies corresponding places in the two molecules.   In cytisine, the oxygen atom exists in the form of neither hydroxyl, nor normal keto-group, nor as a bridge; the assumption that it occupies the same position as in cytisoline renders probable its occurrence as an acetylamino-carbonyl group, as in α-pyridone.   Since cytisine exhibits marked resistance towards reducing agents, the assumption is justified that the two double linkings form a conjugated pair in a single ring.

On the basis of the above considerations, the fourteen possible structures for the cytisine molecule are discussed, the decision in favour of the annexed formula resting on the apparent formation of *iso*valeric acid by the action of barium permanganate on cytisine; this action is to be investigated further when a larger supply of cytisine is available.   The similarity of this structure to that of leucine, which frequently occurs free in the *Papilionaceae*, suggests that this amino-acid may be the parent substance of the cytisine.

Van de Moer's reaction is given by a number of derivatives of 2-pyridone, especially with 1-methyl-2-pyridone, and also, though less intensely, with 1-methyl-2-quinolones and 1-methyl-2-hydroxy-quinolines.   The reaction is also shown by 2-hydroxyquinoline. 2-hydroxy-6-methylquinoline, 2-hydroxy-8-methylquinoline, 2-hydroxy-6 : 8-dimethylquinoline,   2-keto-1 : 6-dimethyl-1 : 2-dihydro-quinoline,   2-keto-1 : 8-dimethyl-1 : 2-dihydroquinoline, and 2-keto-1 · 6 : 8-trimethyl-1 : 2-dihydroquinoline.   Negative results are obtained with hydrocarbostyril, its 1-methyl derivative, and 4-hydroxyquinoline.

1-*Methylhydrocarbostyril*, C_9H_8ONMe, prepared from carbostyril, sodium methoxide, and methyl sulphate, forms an oil, b. p. 165—166°/13 mm., and is difficult to demethylate by means of hydriodic acid.

Zerewitinov's method of estimating active hydrogen gives with cytisine an amount of methane corresponding with one atom of active hydrogen, a similar result being obtained with cytisoline.

T. H. P.

Synthesis of Cytisoline. ERNST SPÄTH (*Monatsh.*, 1919, **40**, 93—128).—Cytisoline (Freund, A., 1904, i, 263) is proved to be 2-hydroxy-6 : 8-dimethylquinoline (compare Ewins, T., 1913, **103**, 97) by the following method. The additive compound obtained by warming 6 : 8-dimethylquinoline with methyl sulphate is oxidised by potassium ferricyanide and aqueous sodium hydroxide solution to 2-*keto*-1 : 6 : 8-*trimethyl*-1 : 2-*dihydroquinoline*, $C_{12}H_{13}ON$, faintly yellow crystals, m. p. 71—72°, which is converted by phosphorus pentachloride and a little phosphoryl chloride at 135—140° into methyl chloride and 2-*chloro*-6 : 8-*dimethylquinoline*, long needles, m. p. 56°. The heating should not be prolonged after methyl chloride ceases to be evolved; if it is continued for six hours, the product is a *dichlorodimethylquinoline*, long needles, m. p. 108—109°. 2-Chloro-6 : 8-dimethylquinoline is converted into 2-hydroxy-6 : 8-dimethylquinoline by heating with water at 240° for two hours, or, better, with methyl-alcoholic sodium methoxide at 100° for forty-five minutes, the resulting 2-methoxy-6 : 8-dimethylquinoline being easily converted into 2-hydroxy-6 : 8-dimethylquinoline by heating with concentrated hydrochloric acid at 210—220° for two hours, or simply by evaporation with hydrochloric acid and subsequent heating on the water-bath.

The identity of 2-hydroxy-6 : 8-dimethylquinoline, m. p. 201—202°, with cytisoline (m. p. 199°, according to Freund, *loc. cit.*) is shown by the m. p. of the mixture, 200—201°, by the conversion of each into identical chloro-, methoxy-, nitro-, and tetrahydro-derivatives, and by the formation of cytisolinic acid from each by oxidation with chromic and acetic acids.

Other substances were examined in the course of the investigation. 4-*Hydroxy*-6 : 8-*dimethylquinoline*, needles, m. p. 221°, softening at 219°, was obtained as follows. 4-*Hydroxy*-2 : 6 : 8-*trimethylquinoline*, m. p. 263—264°, prepared from *m*-4-xylidine and ethyl acetoacetate by Conrad and Limpach's method, was converted in warm methyl-alcoholic solution by methyl sulphate and sodium hydroxide into 4-*methoxy*-2 : 6 : 8-*trimethylquinoline*, pearly leaflets, m. p. 111—112°, which is much more difficultly hydrolysed by hydrochloric acid than are the 2-methoxyquinolines. It reacted with benzaldehyde at 135—140° in the presence of zinc chloride to form 4-*methoxy*-2-*styryl*-6 : 8-*dimethylquinoline*,

$$C_6H_2Me_2\!\!<\!\!\overset{\displaystyle N\!:\!C(CH\!:\!CHPh)}{\underset{\displaystyle C(OMe)}{\rule{2.5cm}{0.4pt}}}\!\!>\!\!CH,$$
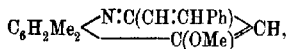
trichroic needles, m. p. 137—138°, which in glacial acetic acid solution containing a little concentrated sulphuric acid was oxidised by potassium permanganate solution, yielding a quinolinecarboxylic acid. This was not isolated in the pure state, but was converted by evaporation with concentrated hydrochloric acid into 4-*hydroxy*-6 : 8-*dimethylquinoline*-2-*carboxylic acid*, m. p. 250° (decomp.), from which 4-hydroxy-6 : 8-dimethylquinoline was obtained by heating in a vacuum at 260—280°. The last compound yielded 6 : 8-dimethylquinoline by distillation with zinc dust, and thus the proof

was furnished that the methyl group in position 2 in 4-methoxy-2:6:8-trimethylquinoline entered into reaction with benzaldehyde.

2-Hydroxy-6-methylquinoline, needles, m. p. 232—233°, and *2-hydroxy-8-methylquinoline*, needles, m. p. 219—220°, were prepared from 6-methylquinoline and 8-methylquinoline respectively in the same way as 2-hydroxy-6:8-dimethylquinoline above; the intermediate compounds are, in the first case, 2-*keto*-1:6-*dimethyl*-1:2-*dihydroquinoline*, crystals, m. p. 84—85°, 2-*chloro*-6-*methyl*-quinoline, needles, m. p. 114—115°, and 2-*methoxy*-6-*methylquino*-line, m. p. 63°, and, in the second case, 2-*keto*-1:8-*dimethyl*-1:2-dihydroquinoline, m. p. 92—93°, b. p. 198—198·5°/13 mm., *2-chloro*-8-*methylquinoline*, needles, m. p. 60—61°, and 2-*methoxy*-8-*methylquinoline*, b. p. 142—143°/18 mm.   C. S.

Harmine and Harmaline. III. and IV. WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON (T., 1919, **115**, 933—967; 967—972).

An Anomaly in the Solubility of Sparteine. A. VALEUR (*Bull. sci. pharmacol.*, 1919, **26**, 145—151).—Mixing aqueous solutions of sodium carbonate and sparteine sulphate results in a slight turbidity, separation of supernatant oily layer, or complete transparency, depending on concentration and temperature. Increase in temperature causes decreased solubility, attributed to the abnormal solubility of basic sparteine sulphate, produced by the action of sodium carbonate on the neutral sulphate. Sparteine alone shows abnormality; 0·496% solution becomes turbid at 12·5°, 0·18% solution at 50°. Solutions of 0·13% or lower do not develop turbidity at the b. p. The solubility is decreased by sodium carbonate, thus in 5% solution, a 0·03% solution of sparteine becomes turbid on boiling. Using progressively regularly increasing amounts of pure sparteine ([α] 2°46') in 5% sodium carbonate, the author found that the temperature at which the solutions began to become turbid was regularly decreased by 2·5° with each increase in 0·01% of sparteine in concentrations between 0·09% and 0·18%, the temperatures ranging between 47·5° and 25°. Above or below these temperatures, irregularities appeared. A curve is presented. Variations in the strength of the carbonate solution caused appropriate variations in the general level of the curves, although they were found to run parallel to that obtained with the 5% sodium carbonate solution. The method consisted in placing the sample in a test-tube with thermometer in a water-bath and observing the exact temperature of the appearing turbidity. It was necessary to work with carefully filtered solutions, to use either a new tube for each test, or to wash the tube with acid, water, and the new solution to be tested. Wide discrepancies of earlier results as to the solubility are due to lack of appreciation of the effect of temperature changes. The author prepared a solution of sparteine sulphate by adding an excess to water at 10·8°, keeping for two days, centrifuging, and filtering, and he determined the solubility by titration

with 0·1*N*-hydrochloric acid, using methyl-orange, by precipitation with silicotungstic acid, by precipitation with picric acid, and by observing the temperature of appearing turbidity in 5% sodium carbonate. The results coincide, and give about 0·32% as the solubility of the compound at 22°. CHEMICAL ABSTRACTS.

Constitution of the Dialkyltetrahydrodipyridyls. BRUNO EMMERT (*Ber.*, 1919, **52**, [*B*], 1351—1353).—It was observed by Hofmann (A., 1881, 921) that unstable, dialkyltetrahydrodipyridyls are formed by the action of sodium amalgam on alkylpyridinium haloids, and it was assumed that the pyridine nuclei were united in the *a*-position. The author has obtained similar substances by the electrolysis of alkylpyridinium salts and by the action of water on sodium pyridine (A., 1909, i, 602; 1917, i, 221), and has therefore endeavoured to deduce their composition with greater certainty. Attempts to reduce *NN'*-dibenzyltetrahydrodipyridyl to the corresponding dipiperidyl were unsuccessful by reason of the tendency of the substance to resinify, but, on distillation with zinc dust, toluene and 4:4'-dipyridyl were obtained. The presence of 2:2'-dipyridyl could not be detected, so that, contrary to Hofmann's assumption, the pyridine nuclei in such compounds are united in the 4-position. H. W.

Isomerism among Derivatives of Indazole. K. VON AUWERS (*Ber.*, 1919, **52**, [*B*], 1330—1339).—The recent communications of Harries (this vol., i, 131) and Freund and Kessler (this vol., i, 283) on isomerisation among heterocyclic bases have induced the author to publish a preliminary account of investigations of a similar nature which are being carried out in his laboratory.

1-Acetylindazole, $C_6H_4\left\langle\begin{smallmatrix}-CH\\NAc\end{smallmatrix}\right\rangle N$, is prepared by the Beckmann transformation of *o*-aminobenzaldoxime, but the yields in different experiments vary greatly; it has m. p. 169—171°, b. p. 191°/ 15 mm. (slight decomp.). The sparingly soluble *nitrate* crystallises in small, shining needles grouped in rosettes, whilst the *compound* with mercuric chloride forms flat, shining needles. 1-Acetylindazole is readily converted by alkali hydroxide or by boiling water into the *N*-acetyl derivative of *o*-aminobenzaldoxime or into the oxime itself. 2-Acetylindazole, $C_6H_4\left\langle\begin{smallmatrix}CH\\N\end{smallmatrix}\right\rangle NAc$, exists in two forms. The stable modification, long, transparent, oblique prisms, m. p. 42—43°, b. p. 260°, is formed by the action of acetic anhydride on indazole, and is rapidly hydrolysed by warm acids or alkali hydroxides; it yields a double *compound* with mercuric chloride. The labile *modification* crystallises in needles or plates, m. p. 106°, and is prepared by the action of acetyl chloride on an ethereal suspension of the silver salt of indazole or by acetylation of indazole with acetyl chloride in the presence of pyridine. It is converted into the stable derivative, m. p. 42°, when distilled under diminished

pressure, by crystallisation from solvents of moderately high boil-
ing point, and, slowly, at the ordinary temperature.

The *N*-alkylindazoles have been investigated by Fischer and Tafel
(A., 1885, 541), who prepared the 2-alkyl derivative by heating
indazole with alkyl iodides. When, however, indazole is heated
with alkyl iodides and sodium in the presence of methyl or ethyl
alcohol, mixtures of 1- and 2-alkylindazoles are obtained, which are
most conveniently separated by fractional distillation followed by
crystallisation of the individual fractions, or, when this is not
possible, by means of the picrates. The course of the reaction is
deduced from a study of the action of ethyl iodide, sodium, and
ethyl alcohol on 3-methylindazole, whereby a mixture of 3-methyl-
1-ethylindazole, b. p. 245·5° (m. p. of picrate, 190—192° or
192—194°, according to the rate of heating), and 3-methyl-2-ethyl-
indazole. b. p. 284—285° (m. p. of picrate, 212—213°), is obtained,
the products being identical with those described by Fischer and
Tafel (*loc. cit.*).   H. W.

Alkyl Derivatives of Indazole-3-carboxylic Acid. K. von
AUWERS and R. DERESER (*Ber.*, 1919, 52, [*B*], 1340—1351).—The
action of various alkylating agents on indazole-3-carboxylic acid and
its esters has been investigated. The behaviour is more complex
than that of indazole itself (preceding abstract). Fortunately, the
widely differing ease of esterification of the alkylindazolecarboxylic
acids affords both a means of fixing their constitution and also of
separating mixtures of them into their components. Thus indazole-
3-carboxylic acid is readily esterified by the Fischer-Speier process,
and this is true of one of the alkylated acids, which is thus a
1-alkyl derivative, whereas the second acid, which can only be
esterified with difficulty, must be the 2-alkyl compound. The esters
of 2-alkylindazole-3-carboxylic acid are obtained by the action of
alkyl iodides on the silver salt of the acid or on the silver com-
pound of the ester.

Direct alkylation of indazole-3-carboxylic acid with alkyl iodide
is not a suitable method, since the substances scarcely react at 100°,
whilst at higher temperatures compounds containing iodine result.
The method may, however, be applied to the esters; thus methyl
indazole-3-carboxylate and methyl iodide at 100° yield a mixture
of methyl 2-methylindazole-3-carboxylate and the corresponding
acid (formed by the action of the liberated hydrogen iodide); the
ethyl ester does not react with ethyl iodide under similar conditions.

2-Alkylindazole-3-carboxylic acids are readily obtained by the
action of methyl or ethyl sulphate and sodium hydroxide on
indazole-3-carboxylic acid, the 1-alkyl isomerides either not being
formed at all or in very small amount. The methyl ester, when
similarly treated, vields, however, a mixture of the 1- and 2-methyl
derivatives. Methyl indazole-3-carboxylate is converted by diazo-
methane exclusively into the 2-methyl compound.

Alkylation with sodium alkoxide and alkyl iodide leads, in
general, to a mixture of isomerides, the relative proportions of

which vary with the particular ester used and also with the alkyl iodide.

The esters of indazole-3-carboxylic acid and its homologues can be distilled without undergoing decomposition, whilst the corresponding free acids eliminate carbon dioxide when heated and yield the indazoles; with the 1-alkyl acids, this happens at the melting point, with the 2-alkyl acids, however, at a higher temperature.

The following individual compounds are described: indazole-3-carboxylic acid, m. p. 260—261°; *methyl* ester, m. p. 168—169°; *ethyl* ester, yellow, shining needles, m. p. 136—137°; *2-methylindazole-3-carboxylic acid*, m. p. 224—225° (decomp.); *methyl* ester, yellow crystals, m. p. 61—62°; *2-ethylindazole-3-carboxylic acid*, small leaflets, m. p. 180—181°; *ethyl* ester, slender needles, m. p. 47—48°, b. p. 179—181°/11 mm.; *1-methylindazole-3-carboxylic acid*, slender needles, m. p. 213—214°; *methyl* ester, colourless needles, m. p. 75—77°; *1-ethylindazole-3-carboxylic acid*, glassy needles, m. p. 162—163°; *ethyl* ester, b. p. 190—192°/10 mm.

H. W.

The Indirubins. J H. MARTINET (*Compt. rend.*, 1919, **169**, 183—185).—The author has prepared a number of substituted indirubins by three different processes, namely, (1) condensation of the isatins with indoxylic acid in slightly alkaline medium in an atmosphere of hydrogen; (2) condensation of the same isatins with 2-anilinoisatin in ammoniacal solution in a current of hydrogen sulphide; by this method, a large part of the product often remains in the mother liquor as a leuco-base, in which case, after filtration, these liquors should be warmed in a current of air; (3) very easily by adding to an acetic acid solution of the isatin, warmed on a water-bath, the technical fusion of phenylglycine.

The following indirubins have been prepared:

From isatin, indirubin itself; from 1-methylisatin, 2-indoxyl-1-methylindole; from 5-bromo-1-methylisatin, *2-indoxyl-3-(5-bromo-1-methyl)indole*, m. p. 265—266°; from 1-ethylisatin, 2-indoxyl-3-(1-ethyl)indole; from 5-bromo-1-ethylisatin, *2-indoxyl-3-(5-bromo-1-ethyl)indole*, m. p. 250—251°; from 5-methylisatin, *2-indoxyl-3-(5-methyl)indole*, m. p. 289°; from 5 : 7-dimethylisatin, *2-indoxyl-3-(5 : 7-dimethyl)indole*, m. p. 337°; from 1 : 7-trimethyleneisatin, *2-indoxyl-3-(1 : 7-trimethylene)indole*, m. p. 252°; from 5-methyl-1 : 7-trimethyleneisatin, *2-indoxyl-3-(5-methyl-1 : 7-trimethylene)-indole*, m. p. 265°; from 5-methyl-1 : 7-a-methyltrimethyleneisatin,

2-indoxyl-3-(5-methyl-1 : 7-a-methyltrimethylene)indole (annexed formula). m. p. 204—205°.
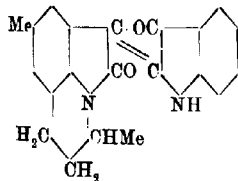
All of these substances are obtained as slender, brownish-violet needles. They give violet-red, alcoholic solutions, the colour of which is rapidly removed on warming with a few drops of potassium hydroxide in the case of those indirubins which have a sub-

stituent attached to nitrogen. [See, further, *J. Soc. Chem. Ind.*, September.] W. G.

Hydurilic Acid and *s*-Dimethylhydurilic Acid. HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1919, **52**, [*B*], 1298—1316).— Hydurilic acid is conveniently prepared by the action of heat on dialuric acid, conversion of the crude product into 5-bromo-5-ethoxyhydurilic acid, and reduction of the latter with stannous chloride. It is also readily obtained by oxidation of barbituric acid in aqueous solution with potassium permanganate, but is not formed from an acid solution. Hydurilic acid is itself further oxidised by permanganate, probably to 5-hydroxyhydurilic acid; the product, however, could not be adequately purified, and, further, could not be reduced to hydurilic acid. *5-Methoxy-hydurilic acid* is readily obtained by the gentle reduction of 5-bromo-5-methoxyhydurilic acid (Biltz, Heyn, and Hamburger, A., 1916, i, 507) by potassium iodide or sodium sulphite, whilst more powerful reducing agents yield hydurilic acid; it forms coarse, hexagonal platelets, which soften at 170° and decompose at 230—240°. With bromine and water, it re-forms bromomethoxy-hydurilic acid, whilst with chlorine it gives 5:5′-dichlorohydurilic acid. *5-Ethoxyhydurilic acid*, prepared in a similar manner, crystallises in pyramids or double pyramids, which decompose at about 242° after becoming red at about 210°. The alkyloxyhydurilic acids are powerful acids; *potassium methoxyhydurilate*, rectangular platelets, is described. The alkyloxy-acids eliminate alcohol when heated, and yield *dehydrohydurilic acid*,

$$CO{<}^{NH \cdot CO}_{NH \cdot CO}{>}C{:}C{<}^{CO \cdot NH}_{CO \cdot NH}{>}CO,$$
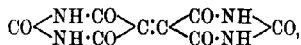
which could not be crystallised without change and which decomposes at about 250°; it appears to be converted in aqueous solution into 5-hydroxyhydurilic acid. The solid acid (but not the aqueous solution) is reduced by potassium iodide to hydurilic acid. With methyl alcohol, chlorine, and bromine, respectively, it yields 5-methoxyhydurilic acid, 5:5′-dichlorohydurilic acid, and 5:5′-*di-bromohydurilic acid*, long, four-sided prisms which evolve bromine at 110° and decompose at 160°. When heated at 120°, the dibromo-acid yields dehydrohydurilic acid, thus exactly resembling 5:5′-dibromotetramethylhydurilic acid; with alcohols, it gives 5-alkyloxy-hydurilic acids, whilst dilute aqueous ammonia converts it into 5-*aminohydurilic acid*, leaflets, decomposing from 70°; the latter is reduced by stannous chloride to uramil and barbituric acid. It reacts with potassium cyanate and molten carbamide, without, however, yielding crystallisable substances. Solid dehydrohydurilic acid also reacts with an aqueous solution of carbamide, giving a *substance*, rectangular platelets, m. p. about 140° (decomp.) after softening at 130°.

5-Methoxy- and 5-ethoxy-tetramethylhydurilic acids are more conveniently prepared by the reduction of 5-bromo-5-methoxy- or

5-bromo-5-ethoxy-tetramethylhydurilic acids with potassium iodide than by the process previously described (loc. cit.); tetramethyl-dehydrohydurilic acid readily reacts with chlorine to yield 5:5'-di-chlorotetramethylhydurilic acid.

Unsuccessful attempts are described to prepare a monomethyl-hydurilic acid by the action of heat on methylalloxantin; the product, however, was hydurilic acid. Similarly, diethylbarbituric acid was found not to condense with dialuric acid.

[In part, with H. Bülow.]—s-*Dimethylhydurilic acid*, rhombic platelets, which decompose at 306—308° after darkening at 270°, is prepared by heating s-dimethylalloxantin at 150°, and is conveniently purified through 5-*bromo*-5-*methoxydimethylhydurilic acid*, which decomposes at 235—240° after softening at 225°. It is converted by methyl sulphate into tetramethylhydurilic acid. 5-*Bromo*-5'-*ethoxydimethylhydurilic acid* forms rhombic platelets decomposing at 206—207°. 5-*Methoxydimethylhydurilic acid*, rectangular platelets, decomposing at 155° after softening at 150°, and 5-*ethoxydimethylhydurilic acid*, rectangular leaflets, which decompose above 300°, are prepared by the reduction of the corresponding bromo-acids with sodium sulphite. The former, when heated under diminished pressure at 150°, gives crude *dimethyl-dehydrohydurilic acid*, which, however, could not be purified; on reduction, it yields dimethylhydurilic acid, whilst bromine transforms it into 5:5'-*dibromodimethylhydurilic acid*, which loses bromine at 80°. 5:5'-*Dichlorodimethylhydurilic acid* is obtained by the action of hydrochloric acid and potassium chlorate on dimethylhydurilic acid; it forms rhombic platelets, which decompose at 295—300° after becoming discoloured from 270°. H. W.

Formation of Cyanic Acid by Oxidation of Organic Substances. Its Identification Based on Quantitative Analysis.

R. Fosse (*Compt. rend.*, 1919, 169, 91—93).—The presence of cyanic acid in solutions of proteins, alone or with dextrose present, and in ammoniacal solutions of amino-acids, glycerol, carbohydrates, or formaldehyde, after oxidation, is shown by isolating it as its silver salt and analysing this salt. The solution after the oxidation is almost completely neutralised with nitric acid and silver nitrate is added. The precipitate is collected at the pump, washed, and extracted with hot water. On cooling the hot extract, the silver cyanate crystallises out, and may be collected and dried. The salt is heated on a water-bath for one hour in ammoniacal solution with ammonium chloride, after which the solution is acidified with acetic acid and the silver chloride is collected on a Gooch crucible and weighed. The carbamide present in the filtrate is estimated by the usual method. W. G.

Ultramicroscopy of Egg-albumin.

J. F. McClendon and H. J. Prendergast (*J. Biol. Chem.*, 1919, 38, 549).—A saturated solution of carefully purified crystalline egg-albumin in distilled

water had a p_H about 4·2, and the ultramicroscope showed only an occasional submicron. On bringing it to $p_H = 4·8$ and re-examining it by the microscope, there was a slight increase in the number of submicrons. This points to the protein existing in true solution, and it is remarked that it seems unfortunate that clear solutions of protein should be classed with suspensoids under the term "colloids."   J. C. D.

The Nomenclature of Blood Pigment and its Derivatives.

WILLIAM DOBINSON HALLIBURTON and OTTO ROSENHEIM (*Biochem. J.*, 1919, **13**, 195—198).—Attention is drawn to the unsatisfactory system of nomenclature of the blood pigments and their derivatives introduced by Hoppe Seyler. As an entirely new system would confuse the literature, it is suggested that a considerable simplification of that at present in use would be effected by the deletion of the ill-chosen name hæmochromogen. It is pointed out that this substance is without doubt identical with reduced hæmatin (Stokes, *Proc. Roy. Soc.*, 1864, **13**, 353). The substance hitherto termed hæmatin should be called oxyhæmatin. This small change renders it possible to show the relationship of the blood pigments and their derivatives by means of a very simple table.   J. C. D.

The Effect of Alcohol on the Digestion of Fibrin and Caseinogen by Trypsin.

EDWARD STAFFORD EDIE (*Biochem. J.*, 1919, **13**, 219—225).—The action of trypsin on fibrin and on caseinogen is affected by dilute alcohol to such different degrees that it is reasonable to suppose either that there are two enzymes concerned in the digestion of these proteins or that different groups of the same enzyme molecule take part in the hydrolysis of the different proteins.   J. C. D.

Additive Compounds of the Halogen Acids with Diphenylarsinic Acid.

V. GRIGNARD and G. RIVAT (*Compt. rend.*, 1919, **169**, 126—129).—When diphenylarsinic acid is dissolved in hydrochloric acid (D 1·17) and the solution allowed to cool, the *hydrochloride*, $AsPh_2O·OH,HCl$, m. p. 134°, is obtained, but if the acid is first diluted with two volumes of water, the *hydrochloride*, $2AsPh_2O·OH,HCl$, m. p. 111—111·5°, is obtained. The first hydrochloride may be converted into the second by warming it in chloroform with an equimolecular proportion of diphenylarsinic acid, whilst the reverse process is brought about by dissolving the second hydrochloride in hydrochloric acid (D 1·17). In a similar manner, two *hydrobromides*, the one, $AsPh_2O·OH,HBr$, m. p. 126—126·5°, the other, $2AsPh_2O·OH,HBr$, m. p. 119·5—120°, have been obtained. The hydrobromides are less stable than the hydrochlorides.

[By CH. MAUGUIN.]—The crystallographic measurements for these addition compounds, all of which crystallise in the monoclinic system, are: the hydrochloride, $AsPh_2O·OH,HCl$, has $a:b:c =$

$0.8063:1:?$, $\beta=109°25'$; the hydrochloride, $2AsPh_2O\cdot OH,HCl$, has $a:b:c=0.6346:1:0.801$, $\beta=94°30'$; the hydrobromide, $AsPh_2O\cdot OH,HBr$, has $a:b:c=0.790:1:?$, $\beta=108°26'$; the hydrobromide, $2AsPh_2O\cdot OH,HBr$, has $a:b:c=0.6333:1:0.779$, $\beta=93°56'$. W. G.

Physiological Chemistry.

Relation between the Electric State of the Cell Wall and its Permeability to a Given Ion. PIERRE GIRARD (*Compt. rend.*, 1919, **169**, 94—97).—The author has shown that, by modifying the charge on the cell wall in the case of blood corpuscles, its permeability to chlorine ions is also modified. In suspension in 0·9% sodium chloride solution, the corpuscles neither absorb nor emit chlorine, but in a similar solution acidified with lactic acid, taking into account the expansion of the corpuscles, it is shown that chlorine passes in, due to the electrification of the cell wall by the hydrogen ions of the acid. This positive charge induced by the hydrogen ions on the cell walls is partly annulled if the acid used has a high valency, as is shown by replacing the lactic acid with citric acid. The presence in the sodium chloride solution of a non-toxic, alkaline salt, such as potassium carbonate, tends to increase the negative charge on the cell wall, and chlorine, instead of passing into the cell, passes out. W. G.

Effect of Diet on the Alkaline Reserve of the Blood. J. F. MCCLENDON, L. VON MEYSENBUG, O. J. ENGSTRAND, and FRANCES KING (*J. Biol. Chem.*, 1919, **38**, 539—548).—The alkaline reserve in man and the dog appears to be very resistant to the influence of the diet. In the case of the rabbit, however, changes due to diet or starvation were noted. J. C. D.

The Action of Ultraviolet Rays on the Accessory Food Factors. SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1919, **13**, 164—171).—The accessory food factor present in butter is inactivated by exposure to ultraviolet light for eight hours. This treatment also bleaches the butter and renders it quite unfit for consumption. The antineuritic and antiscorbutic vitamines are not destroyed by ultraviolet rays. J. C. D.

Relationship of the Pancreatic Enzymes. FREDERIC FENGER and MARY HULL (*J. Biol. Chem.*, 1919, **38**, 487—500).—The normal pancreas as removed from the animal is of distinctly acid reaction and possesses high diastatic, considerable lipolytic, and

some proteolytic activity. The first-named enzyme is present in fully activated form, but increased lipolytic activity and proteolytic activity are obtained by the addition of bile and duodenal mucosa respectively. By the addition of adequate amounts of these two substances, it is possible to produce and maintain maximum activity of the three enzymes in the removed pancreas.   J. C. D.

The Colours of Colloids. VII. Blue Feathers. WILDER D. BANCROFT (*J. Phys. Chem.*, 1919, **23**, 365—414. Compare this vol., i, 421).—The colours in feathers fall into three categories. Of these, only black, brown, reddish-orange, and yellow are objective chemical colours directly produced by pigment. A second type is structural, notably blue and violet, which are produced by finely divided air bubbles in a specially constructed, transparent layer of thick-walled "box cells" lying below the epidermal cells, which behave in a manner similar to the dust in the atmosphere, and the effect of which is intensified by a brownish-black pigment layer behind. Lastly, there are colours which depend entirely on the position of the light and eye, which are produced by a transparent sheath which acts like a prism. The combination of the structural blue with a yellow pigment gives a structural green. By displacing the air in the "box cells" with a medium of the same refractive index as the cell wall, such as Canada balsam or benzene, the structural blue colour disappears.   G. F. M.

The Non-protein Nitrogenous Constituents of Cow's Milk. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1919, **38**, 453—458). —Analyses of the total non-protein nitrogen, amino-nitrogen, urea, uric acid, creatine, and creatinine in cow's milk are given. The content of the first three is influenced by the character of the food, being increased in high protein feeding. High figures for these fractions are also found for colostrum.   J. C. D.

The Peroxydases in Milk. H. VIOLLE (*Compt. rend.*, 1919, **169**, 248—250).—It is shown from an examination of the mammary glands of guinea-pigs that the peroxydase is contained in the glandular cells, and in the case of a healthy mammal, therefore, not submitted to violent treatment, the fresh milk may contain little or no peroxydase. On the other hand, the milk coming from an animal having any affection of the mammary gland may be rich in peroxydase. Similarly, milk which has been heated at 78—80°, and in which, therefore, the peroxydase has been destroyed, may have the latter restored by the addition of fresh organic tissues or liquids of animal or vegetable origin containing them. The peroxydase test is not therefore trustworthy as a means of distinguishing between fresh and heated milk.   W. G.

Mechanism of the Toxic Action of Urease. P. CARNOT and P. GÉRARD (*Compt. rend.*, 1919, **169**, 88—90. Compare *Compt. rend. Soc. Biol.*, 1919, April).—The toxicity of soya flour when

injected intravenously or subcutaneously is shown to be due to the action of the urease present in it. In the case of dogs receiving an intravenous injection, it was found that the carbamide present in the blood disappeared very rapidly, although in some cases it reappeared later. The ammoniacal nitrogen content of the blood and organs increased progressively. The phenomena of cerebral intoxication are due to the localisation of ammonia in the brain, this being produced by the action of the urease on the carbamide of the blood and tissues. W. G.

Chemistry of Vegetable Physiology and Agriculture.

The Preparation of Silica Jelly for Use as a Bacteriological Medium. ALBERT T. LEGG (*Biochem. J.*, 1919, **13**, 107—110).—The success of the method depends on the use of a rather thick collodion dialysing membrane of low permeability, a sufficiently long period being given for the sodium silicate and hydrochloric acid to react after mixing, and the use of distilled water for dialysing. When the product is to be used for culture purposes, it is advisable that tubing and autoclaving should follow immediately after dialysing. J. C. D.

The Vitamine Requirement of Yeast. A Simple Biological Test for Vitamine. ROGER J. WILLIAMS (*J. Biol. Chem.*, 1919, **38**, 465—486).—Attempts to grow pure cultures of yeast in synthetic media from a single cell failed, a finding which recalled the experiments of Pasteur and of Wildiers ("La Cellule," 1901). Further experimentation largely confirmed Wildiers' results, and the possibility of the substance termed "bios" by that author being identical with the water-soluble *B*-vitamine presented itself. It was found that the substance which stimulates the growth of yeast occurs in many of the materials which are known to be sources of water-soluble *B*, and, moreover, the properties of the two substances showed close resemblance. The former substance was not identified as any one of the amino-acids obtained from caseinogen. It is believed that there is justification for concluding that the two substances, Wildiers' "bios" and the so-called water-soluble *B*, are identical. J. C. D.

Preparation of Glycerol by Fermentation. W. CONNSTEIN and K. LÜDECKE (*Ber.*, 1919, **52**, [*B*], 1385—1391).—The experiments were undertaken with the object of providing the Central Powers with a means of obtaining glycerol after the importation of fats had been prevented by the blockade.

Glycerol is formed to the extent of about 3% in the ordinary

fermentation of sugar, and the yield is considerably increased when fermentation is effected in the presence of slightly alkaline salts, which do not poison the yeast. In these circumstances, however, the solutions are very liable to infection, thereby decreasing the yield of glycerol; in this connexion, sodium sulphite is very useful, since, particularly at high concentrations, it has an antiseptic action and especially hinders the development of the lactic acid bacilli, whilst also it gives the highest yields of glycerol. The latter vary from 23·1% when the weight of sulphite used is 40% of that of the sugar to 36·7% with twice the weight of the sugar; too large an addition of sodium sulphite causes fermentation to be too slow or damages the yeast. The process does not appear to depend on the particular variety of fermentable sugar (refined sugar, crude sugar, or molasses can be used) or on the species of yeast. The latter, which does not increase to more than a slight extent during the sulphite fermentation, can be utilised for further experiments after subjection to a "purification fermentation" in slightly acid solution. The glycerol, after suitable purification, is adapted not only to nitration, but also to pharmaceutical purposes; occasionally it contains small amounts of trimethyleneglycol, probably due to secondary decomposition of glycerol by bacteria.

The volatile products of the fermentation consist chiefly of ethyl alcohol and acetaldehyde. Increase in the quantity of sulphite diminishes the production of alcohol and carbon dioxide and increases that of glycerol and acetaldehyde.

With regard to the mechanism of the reaction, two factors appear to be involved, a general action of salts and a specific sulphite action. Increased production of glycerol occurs in the presence of considerable quantities, not only of slightly alkaline salts, but also of certain neutral or acid salts (calcium chloride, ammonium chloride, sodium chloride, sulphate or nitrate, ferrous sulphate, aluminium sulphate). The specific action of the sulphite is possibly connected with its relationship to aldehydes.   H. W.

The Vegetable Proteases. I. Introductory. ERNEST ARTHUR FISHER (*Biochem. J.*, 1919, **13**, 124—134).—The presence of proteinoclastic and peptoclastic enzymes in a number of green plants (cereals in the grass stage, leguminous plants, buckwheat, and white mustard) has been established. A detailed examination of beans, field peas, and buckwheat indicated that all parts of the plant are active in this respect at all stages of growth. The proteinoclastic and peptoclastic action of the leaves increases with increasing maturity, and does not fall off after the flowering stage. There is a distinct increase in the activity of these enzymes after germination. The suggestion is advanced that the peptoclastic action of green fodder plants is sufficiently great to be of assistance to the animal organism in the digestion of the simple protein substances.   J. C. D.

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General and Physical Chemistry.

The Infra-red Spectrum of Iron. H. M. RANDALL and E. F. BARKER (*Astrophys. J.*, 1919, **49**, 42—47).—The region investigated extended from 9000 to 30,000 Å., and was found to contain some fifty measurable lines. The experimental arrangement was the same as that previously described (Randall, A., 1910, ii, 1014). The slit of the collimator and the thermopile were at first approximately 0·2 mm. wide, and covered a region in the neighbourhood of $1\,\mu$ of about 6 Å. and at $3\,\mu$ of about 3·7 Å. Later the entire spectrum was examined with a slit 0·5 mm. wide, and a very appreciable number of weaker lines were found and measured. No systematic differences between the values of wave-lengths measured with the slits of different width were noted. The material used in the major part of the work was ingot iron (99·8% Fe), the largest single impurity being copper, approximately 0·04%. Electrolytic iron also was used. No lines due to impurities in either were observed. The iron was placed in a boring in the positive carbon (1·9 cm.), the hole being as large as the carbon would permit. The carbons showed several infra-red potassium lines and also two others, the approximate values of which are 11,439 Å. and 10,692 Å. The origin of these lines is not known. The current used was in general greater than 60 amps. Tables of wave-lengths are given in Ångström units, as measured in air according to the Rowland scale. The relative intensities of the lines were estimated from the galvanometer deflexions. For the region between $0·8\,\mu$ and $1\,\mu$ the photographic method is more sensitive than the bolometric, but beyond $1\,\mu$ the latter becomes increasingly the more sensitive.

CHEMICAL ABSTRACTS.

The Infra-red Spectra of Cobalt, Nickel, Manganese, and Chromium. H. M. RANDALL and E. F. BARKER (*Astrophys. J.*, 1919, **49**, 54—60. Compare preceding abstract).—The experimental arrangement and methods were the same as those for the iron spectrum. With the exception of manganese, which volatilised readily and gave a comparatively steady arc, the metals were very similar to iron in their action in the arc. Nickel and cobalt produced possibly an even more uncertain arc than iron. The strongest lines were given by manganese. The materials used were "pure" metals of commerce. No lines due to any of the impurities likely to be found were actually observed. The currents used were 60—80 amps. The spectrum of each metal was in general searched twice, once with narrow slits and once with double width slits. A number of the lines in the tables are multiples of strong lines of short wave-lengths. It is thought, however, that in each case it has been established that the higher order line of short wave-length is superposed by a line of long wave-length of the first order.

CHEMICAL ABSTRACTS.

The Applications of Beer's Law in Organic Chemistry.
E. J. E. HÜFFER (*Chem. Weekblad*, 1919, **16**, 720—734).—A discussion of Beer's law of light absorption and its application to the determination of various cases of isomerism and polymerism in organic chemistry. Special reference is made to the colour theory of Hantzsch.   W. S. M.

The X-Ray Spectra of the Elements. M. DE BROGLIE (*Compt. rend.*, 1919, **169**, 134—136).—The author has measured the frequency difference of the α- and β-rays in the K-spectrum of rhodium, and from these values has calculated the fundamental frequency of interval of Sommerfeld (*Ann. Physik*, 1916). He obtains the value $\Delta \nu_H = 0.369$, which is in close agreement with Paschen's figure (*loc. cit.*).

He has measured the wave-lengths of the first two L-bands in the absorption spectrum of radium, the results being: band L_1, $\lambda = 0.802 \times 10^{-8}$ cm.; band L_2, $\lambda = 0.670 \times 10^{-8}$ cm. The latter figure is a correction of one previously given (compare this vol., ii, 207).   W. G.

Relation between General X-Radiation and the Atomic Number of the Target. W. DUANE and T. SHIMIZU (*Physical Rev.*, 1918, **11**, 491—492).—The intensity of the general X-radiation is proportional to the atomic number, and not to the atomic weight of the radiator. The apparatus used was a rotating target on which were mounted quadrants of iron, cobalt, nickel, and copper. The current produced by ionisation in a chamber containing methyl iodide was:

Ion-current (volts/sec.).

Volts.	Cu (29).	Ni (28).	Co (27).	Fe (26).
19,140	0·0124	0·0120	0·0114	0·0110
32,400	0·1327	0·1295	0·1251	0·1210

The numbers in parentheses are the respective atomic numbers. Cobalt occupies a position between iron and nickel, according to its atomic number as determined by Moseley, but not according to its atomic weight, which is anomalous.   CHEMICAL ABSTRACTS.

The Structure of Radioactive Elements. INGO W. D. HACKH (*Physical Rev.*, 1919, **13**, 165—170).—Partial atomic structures of the elements in the periodic table between uranium and lead, on the basis of the radioactive disintegration series, are suggested. The emission of the α-particle causes the change of position of two electrons from the valency ring to an interior unstable ring, and the emissions of the β-particle the change of one electron in the opposite sense. This is referred to as a theory of metastasic electrons, and it supports the view that the seat of disintegration is not in the outer or valency shell, but in the next inner shell, and is caused by the shifting of two electrons.   F. S.

"Old Age" of Chemical Elements. INGO W. D. HACKH (*Science*, 1919, **49**, 328—329).—A discussion based on Richards'

work on radioactive lead (A., 1914, ii, 453; 1917, ii, 91). The author states that "all other elements should be subject to an increase in mass, and it could therefore be predicted that, for example, helium of the atmosphere and of minerals will have an 'atomic weight' which is 0·0214 higher than the atomic weight of helium from radioactive disintegration, that is, there should be an 'old' or 'common' helium with atomic weight of about 3·94, and a 'neo' helium of atomic weight 3·92."

CHEMICAL ABSTRACTS.

Phenomena of Electrolytic Luminescence shown by certain Metallic Anodes. I. JAMES LAVAUX (*Compt. rend.*, 1919, **169**, 180—182).—Certain metals capable of giving, with the electrolytic anion, insoluble, adherent salts, which are non-conductors, show luminous phenomena correlative with a state of intense anodic polarisation. Of the metals studied, iron, copper, cadmium, and lead do not show any luminous phenomena and show no tendency to anodic polarisation. On the other hand, aluminium, magnesium, zinc, and bismuth show both. The luminous phenomena may be of two types, namely, phosphorescence and sparking. The first three metals show both types, but bismuth only shows sparking. The phenomena of electrolytic phosphorescence only appear in very short electric fields of high intensity, and are connected with high polarisation of the anode and the creation at its surface of an intense electric field. The phosphorescence is not accompanied by noise or sparking, and only occasions a minute expenditure of current and a very feeble development of heat. On the other hand, the sparking appears to characterise an abnormal working of the apparatus. It occurs in two forms: (1) more or less numerous, small, brilliant sparks; (2) a rain of fire giving the anode the appearance of a star-spangled sky in a state of continuous transformation. The sparking is due to the momentary rupture of the isolating layer at points where, for a few moments, a current sufficiently intense to volatilise a liquid film passes, whence interruption, sparking, and crepitation.

Of the four metals exhibiting these phenomena, aluminium is the best for their study.   W. G.

The Melting Points of Mixtures of Organic Compounds. RICHARD MEYER and WILHELM MEYER (*Ber.*, 1919, **52**, [*B*], 1249—1255).—The melting point of an organic compound is, in general, depressed by admixture with a second substance; the authors have previously shown that this is not the case with the tribromo-compounds of mesitylene and ψ-cumene (this vol., i, 72), and now describe a series of similar observations with the following compounds: tetrabromo-o-xylene and tetrabromo-m-xylene; tetrabromo-m-xylene and tetrabromo-p-xylene; tetrabromo-o-xylene and tetrabromo-p-xylene; tetrabromo-o-, -m-, and -p-xylenes; dibromodurene and dibromoisodurene; thiophen picrate and thionaphthen picrate; thionaphthen picrate and naphthalene picrate; thiophen

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picrate and naphthalene picrate; α- and β-methylnaphthalene picrates; β-methylnaphthalene and naphthalene picrates; mono-chloro- and monobromo-hydroxyhydrindenes. The phenomena have been more exhaustively investigated with the methylnaphthalene picrates and with naphthalene and β-methylnaphthalene picrates. The melting points of synthetic mixtures were determined in capillaries on the one hand and by determining the temperature of solidification on the other, similar, but not identical, results being obtained by either method. In the case of naphthalene and β-methylnaphthalene picrates, a depression is not observed, but the melting point rises sharply when more than 33% of the former is present; with α- and β-methylnaphthalene picrates, a slight depression occurs until the concentration of the former attains about 16%, after which the melting point rises. In both cases, the authors consider that mixed crystals are formed.   H. W.

A Modification of the Freezing-point Method for the Determination of Molecular Weights. H. J. PRINS (*Chem. Weekblad*, 1919, **16**, 929—931).—The determination of the mole-cular weight of substances containing hydroxyl by means of the depression of the freezing point in benzene solution is rendered difficult owing to the association of the solute. In such cases, a number of freezing-point measurements are made, each after successive additions of about 2 c.c. of benzene from a burette. The degree of association decreases with increasing dilution, and the true molecular weight is easily obtained by graphical extrapolation.
W. S. M.

A New Form of Distilling Bulb. J. S. McHARGUE (*J. Ind. Eng. Chem.*, 1919, **11**, 670—671).—A new form of distilling bulb can be made from sections of glass tubing of different diameter. A bulb is blown on the end of the larger tube, and in the base of this a hole is blown to receive the top of the smaller tube, which has been made in the form of a T-tube with its arms open and deflected downwards. This is sealed into the tube, two small openings being left near the ends of the T-piece to allow condensed water to flow back into the interior of the distilling flask. The other end of the larger tube is bent twice at right angles, and is connected with the condenser. By the use of this bulb, soap bubbles are broken up, and the contents of the distilling flask cannot be carried over mechanically. A further advantage is that the steam issuing from the two ends of the T-piece into the bulb keeps the latter at a uniform temperature and accelerates the distillation.   C. A. M.

The Density of the Saturated Vapour of Propyl Acetate and the Density of the Liquid which Emits this Vapour. E. ARIÈS (*Compt. rend.*, 1919, **169**, 216—219).—In the formulæ previously given for the molecular volumes of the saturated vapour and the liquid which emits it (see this vol., ii, 184), the values of the function a were not known. The author now deduces a formula

for calculating the values of a, and by means of it calculates the values of ν_1 and ν_2 for propyl acetate over a temperature range from 90° to 276·2°. The results are in close accord with those observed by Young. W. G.

The Use of Turpentine Resin in Turpentine as a Foam Breaker. E. C. KENDALL (*J. Biol. Chem.*, 1919, **38**, 529).—A 20% solution of resin in turpentine is a most efficient foam breaker. The solution should be neutral to alizarin. J. C. D.

Equilibrium in the System Na_2SO_4–$CuSO_4$–H_2SO_4–H_2O. H. W. FOOTE (*J. Ind. Eng. Chem.*, 1919, **11**, 629—631).—At a given temperature, univariant systems of three components have two solid phases in equilibrium with a solution of definite composition and vapour pressure, whilst in the case of systems of four components there are three solid phases at such points. To determine the univariant points in systems of three components, a series of crystallisations at the given temperatures was made. When one compound was deposited near the point where another was formed, an excess of the latter, or in some cases of both compounds, was added, and the solubility of the mixture determined. After the univariant points in a ternary mixture had been obtained, the corresponding points in a quaternary mixture were found by adding an excess of the third solid. In determining the changes which take place when sulphuric acid is added in increasing amounts, up to 60%, to the system Na_2SO_4–$CuSO_4$–H_2O, the solubilities of the univariant systems were determined, and the points graphically represented were connected with straight lines to show the composition of the corresponding bivariant systems. In the case of solutions containing the four components, copper was estimated electrolytically, sodium as sulphate after removal of the excess of sulphuric acid by ignition with ammonium carbonate, and free sulphuric acid by titration with sodium hydroxide solution.

System Na_2SO_4–H_2SO_4–H_2O.—The results obtained at 25° agreed substantially with those of D'Ans (A., 1906, ii, 351), although no evidence of the formation of the hydrate, $Na_3H(SO_4)_2,H_2O$, which D'Ans found to be rarely formed, was obtained. At 12°, the following compounds separated: $Na_2SO_4,10H_2O$, $Na_2SO_4,10H_2O$ and $Na_3H(SO_4)_2$, $Na_3H(SO_4)_2$ and $NaHSO_4,H_2O$, $NaHSO_4,H_2O$. At 25°, the solubility relationships are more simple, for at 12° the anhydrous salt is not stable under any conditions, and the decahydrate exists in equilibrium with the salt $Na_3H(SO_4)_2$ at the univariant point (see also Pascal, A., 1917, ii, 248).

System $CuSO_4$–H_2SO_4–H_2O.—In this system no acid salt is formed, but the sulphuric acid dehydrates the pentahydrate, yielding successively the trihydrate, monohydrate, and, finally, the anhydrous salt, in concentrated sulphuric acid.

System Na_2SO_4–$CuSO_4$–H_2O.—A transition temperature was observed at 16·7°, below which only a single salt crystallised. At 12° there is only a univariant system with two solid phases,

$Na_2SO_4,10H_2O$ and $CuSO_4,5H_2O$. At 25° there are two such systems, in one of which the solid phases consist of the double salt $Na_2SO_4,CuSO_4,2H_2O$ and $CuSO_4,5H_2O$, whilst in the other they consist of the double salt and $Na_2SO_4,10H_2O$.

System Na_2SO_4–$CuSO_4$–H_2SO_4–H_2O.—At 12° the two salts in water crystallise separately, but when more than 7·4% of sulphuric acid is present, the double salt forms, and at this concentration the univariant system contains the three solid phases of the two single salts and the double salt. In the presence of this proportion of sulphuric acid, the double salt is stable below its transition temperature. Equilibrium in the system $CuSO_4,5H_2O$–$Na_2SO_4,10H_2O$–double salt is reached very slowly at 12°, and the two single salts can remain in contact with a solution containing more than 7·4% of sulphuric acid for a considerable time without forming the double salt. The other systems soon attained equilibrium. At 12° the solid phases were as follows: (1) $Na_2SO_4,10H_2O$, $Na_3H(SO_4)_2$, double salt with 16·50% sulphuric acid in solution. (2) $Na_3H(SO_4)_2$, $NaHSO_4,H_2O$, double salt with 27·97% sulphuric acid. (3) $NaHSO_4,H_2O$, double salt (bivariant) with 58·2% sulphuric acid. (4) $CuSO_4,5H_2O$, $CuSO_4,3H_2O$, double salt with 50·54% sulphuric acid. (5) $CuSO_4,3H_2O$, $CuSO_4,H_2O$, double salt with 59·96% sulphuric acid. (6) $Na_2SO_4,10H_2O$, $CuSO_4,5H_2O$, double salt with 7·40% sulphuric acid. The results obtained at 12° and 25° are plotted in diagrammatic form, and show the instability of the sodium hydrogen sulphates in presence of copper sulphate, which converts them into the double salt.

C. A. M.

Action of Sulphuric Acid on certain Organic Compounds of Homologous and Isomeric Series. JAROSLAV MILBAUER and ANTONÍN NĚMEC (*J. pr. Chem.*, 1919, [ii], **99**, 93—105).— The authors have made experiments to ascertain the influence exerted by the constitution of organic compounds on the velocity of their oxidation by sulphuric acid. In each case, 4×10^{-4} gram-mols. of the compound were heated with 25 c.c. of the concentrated acid, this giving a column of liquid 9·5 cm. in height. The temperature was usually kept at 200°, but in some cases in which the velocity of reaction was very low, temperatures as high as 230° were employed. The sulphur dioxide formed was expelled by means of a current of carbon dioxide and its amount determined.

The aldoses are more difficult to oxidise than the corresponding polyhydroxy-derivatives, with the exception of mannitol, which in very small amounts (0·00004 mol.) retards the combustion of carbohydrates, without, however, affecting the final stage reached; mannitol thus acts as a true negative catalyst. The methylated carbohydrates undergo more profound combustion than the corresponding aldoses or alcohols containing the same number of carbon atoms; increase in the number of hydrogen atoms united to a carbon atom is accompanied by increase in the amount of sulphur dioxide formed. With isomeric sugars, steric configuration has no

influence on the combustion, and with di- and tri-saccharides, although these are not completely burnt, the amount of sulphur dioxide formed is equal to the sum of the amounts yielded by the constituent monosaccharides; the latter also do not undergo complete combustion. Mercuric sulphate not only acts as a positive catalyst, but increases the total quantity of sulphur dioxide; with 0·0001 gram-mol. of the salt, the increase amounts to 9% in the case of sucrose.

Dicarboxylic acids of the type $CO_2H\cdot[CH_2]_n\cdot CO_2H$ give with sulphuric acid at 200° only small amounts of sulphur dioxide, this resulting from decomposition of the acids with formation of carbon dioxide and monoxide, followed by reaction of the latter with the sulphuric acid, $CO + H_2SO_4 = CO_2 + SO_2 + H_2O$.

The unsaturated acids are very easily attacked, scission occurring first at the double linking. Aliphatic acids, such as oleic and fumaric acids, are oxidised far more rapidly than aromatic acids like cinnamic acid; aromatic hydroxy-acids (salicylic) are not oxidised by sulphuric acid at 200°. With the dicarboxylic acids of the aliphatic series, neither the velocity of combustion nor the amount of sulphur dioxide formed depends on the number of hydroxy-groups in the molecule, the reaction being determined in each case by the special chemical structure of the acid; here also mannitol acts as a true negative catalyst, whilst mercuric sulphate not only accelerates the oxidation, but carries it to a further extent.

With the amino-acids, the quantity of sulphur dioxide formed and the velocity of the combustion increase with the molecular weight; mannitol, and also boric anhydride, act as negative catalysts, and mercuric sulphate exerts the action described above. In the case of the aromatic hydrocarbons, the combustion proceeds further as the number of carbon-containing groups attached to the benzene nucleus increases.

Of the dihydroxybenzenes, the para-compound is oxidised the most rapidly and the meta-compound the most slowly, this behaviour being analogous to the reducing powers of these compounds when employed as photographic developers. None of the trihydroxybenzenes is oxidised as rapidly as it would be if one of the three hydroxy-groups were removed, but the rule holding with the dihydroxy-derivatives is obeyed; thus, pyrogallol represents a combination of two ortho-positions, hydroxyquinol one of an ortho- and a meta-position, and phloroglucinol one of two meta-positions. α-Naphthol is more rapidly oxidised than β-naphthol. With the quinones, the combustion is the more rapid the smaller the number of substituent groups in the $O\dot:C_6H_4\dot:O$ nucleus.   T. H. P.

Derivation of the Law of Even Atomic Numbers. ERNST MOHR (*J. pr. Chem.*, 1919, [ii], **99**, 106—108).—If in any molecule the numbers of uni-, bi-, . . . sexa-valent atoms are a, b, . . . f respectively, the sum of all the valencies is given by $\Sigma V = a + 2b + 3c + 4d + 5e + 6f$. On the assumption that no valency in the mole-

cule remains unsaturated, the sum of all the linkings in the mole-
cule is represented thus: $\Sigma B = \Sigma V/2 = b + 2d + 3f + (a + 3c + 5e)/2$.
Since both ΣB and $(b + 2d + 3f)$ are positive integers, the term
$(a + 3c + 5e)/2$ must also be a positive integer. Further, as $(c + 2e)$
is a positive integer, the expression $(a + 3c + 5e)/2 - (c + 2e)$, that is,
$(a + c + e)/2$, must also be a positive whole number, and $(a + c + e)$
a positive, even integer; this is the law of even atomic numbers. A
similar proof holds for the case when septa- and octa-valent atoms
are present in the molecule.

With substances like triphenylmethyl, $C_{19}H_{15}$, in the molecule of
which one valency is unsatisfied, the law holds only if one of the
carbon atoms is regarded as tervalent.

This law is often useful in indicating the possibility or otherwise
of particular molecular formulæ.   T. H. P.

Inorganic Chemistry.

The Solubility of Iodine in Water-Alcohol Mixtures. N.
SCHOORL and A. REGENBOGEN (*Pharm. Weekblad*, 1919, **56**,
538—545).--The results of solubility determinations of iodine in
water-alcohol mixtures as given in the literature are generally
much too high, on account of the formation of hydriodic acid during
the prolonged contact of the iodine with the solvent. The authors
eliminate this source of error by preparing a nearly saturated solu-
tion of iodine in absolute alcohol. A weighed quantity of this is
mixed with a weighed quantity of water, and. after shaking, a
portion of the solution is drawn through a filter into a pipette and
weighed. Potassium iodide solution is added and the iodine
titrated with thiosulphate.   W. S. M.

Effect of a Film of Oil on the Aeration of Water.
HERBERT F. STEPHENSON (*Analyst*, 1919, **44**, 288).--Water covered
with a layer of petroleum oil 0·6 cm. in depth absorbs oxygen
from the atmosphere at the same rate as does water not covered by
oil.   W. P. S.

**Fluorosulphonic Acid, Fluorosulphonates, and Sulphuryl
Fluoride.** WILHELM TRAUBE, J. HOERENZ, and F. WUNDERLICH
(*Ber.*, 1919, **52**, [B], 1272—1284).--It has been previously shown
that ammonium fluorosulphonate can be prepared by the action of
sulphur trioxide on ammonium fluoride (A., 1913, ii, 947); the
further investigation of this and similar substances is described in
the present communication.

Ammonium fluorosulphonate is most conveniently prepared by
the gradual addition of dry ammonium fluoride to sulphuric acid

containing about 70% of sulphur trioxide, and treatment of the product with a small excess of ammonia dissolved in methyl alcohol. The salt has m. p. 245° and readily reacts with gaseous ammonia, particularly at low temperatures, with formation of liquid ammines. The alkali fluorosulphonates are prepared by the action of the requisite alkali hydroxide on the ammonium salt in aqueous solution; the *potassium* salt, short, stout prisms, m. p. 311°, the *rubidium* salt, m. p. 304°, the *lithium* salt, long, shining needles ($+3H_2O$), m. p. 60—61° or m. p. about 360° (anhydrous), are described. All the fluorosulphonates are freely soluble in water, with the exception of the *nitron* salt. The *barium* salt was not obtained in the pure form. The fluorosulphonates are unexpectedly stable towards water, from which they can be crystallised if the operation is rapidly performed; in the presence of mineral acids, they are readily hydrolysed to hydrofluoric and sulphuric acids, but are much more stable in alkaline solution. With aqueous ammonia, they yield chiefly aminosulphonates (compare this vol., i, 434).

The alkali fluorosulphonates are very stable towards heat; thus, when the potassium salt was heated for some time to bright redness, it only suffered slight decomposition, with the evolution of sulphur dioxide, sulphur trioxide, hydrogen fluoride, and oxygen. Crude barium fluorosulphonate, on the other hand, is decomposed at a red heat into barium sulphate and sulphonyl fluoride, this being the most convenient method of preparing the latter.

The formation of fluorosulphonates by heating mixtures of fluoride and pyrosulphates has been further investigated; the best yields are obtained from potassium pyrosulphate and an excess of ammonium fluoride; the yield is appreciably less when the latter is replaced by potassium fluoride, and still poorer when sodium fluoride is used. Fluorosulphonates are also obtained by heating mixtures of ammonium persulphate with fluoride, or by compressing fluoride and pyrosulphate, particularly in the presence of a little water.   H. W.

Reaction of Thiosulphate with Iodine. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 572—585).—In neutral or weakly acid solution, the reaction between iodine and thiosulphate takes place according to the equation $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$. In weakly alkaline solutions, part of the thiosulphate is oxidised directly to sulphate without the intermediate formation of tetrathionate. The side reaction may be represented in two stages: $I_2 + OH' = HOI + I'$, followed by $4HOI + S_2O_3'' + 6OH' = 2SO_4'' + 4I' + 5H_2O$. In sufficiently strongly alkaline solution, all the thiosulphate may in this way be oxidised to sulphate. In strongly acid solution, the reaction is as in neutral solution, the decomposition of the thiosulphate by the acid being slow in comparison with the formation of tetrathionate.   W. S. M.

Electrolytic Preparation of Colloidal Selenium. A. GUTBIER and G. L. WEISE (*Ber.*, 1919, **52**, [*B*], 1374—1378).— When a dilute, aqueous solution of selenium dioxide is electrolysed

between platinum poles (preferably in the presence of a trace of alkali) with a tension of 220 volts, a moderate evolution of gas which does not contain hydrogen selenide is first observed; as soon, however, as the solution attains its boiling point, the formation of colloidal selenium commences, and the solution becomes consecutively yellow, yellowish-red, red, bluish-red, and finally blue. Selenium is not deposited in an irreversible form until the latter stage is reached provided that the original solution is not too concentrated. The yellow systems become yellowish-red when cooled, and can be preserved, even if not dialysed; they can readily be purified by dialysis, are not decomposed by filtration through paper, and can be considerably concentrated by evaporation over a free flame. The yellowish-red solutions sometimes retain their colour and at other times become red when cooled; in the former case, they can be purified by dialysis, and then behave in the same manner as the yellow solutions. The red solutions invariably show a tendency to become bluish-red when cooled—a sign of incipient coagulation; they can only be obtained in a moderately stable condition if dialysed while still hot, and then immediately diluted with pure water or with a solution of a protective colloid, such as gum arabic. The bluish-red and the blue solutions decompose generally when cooled, invariably during dialysis or when preserved at the ordinary temperature. All the dialysed solutions are very sensitive towards electrolytes; red precipitates are thus obtained which pass into the black or grey modification of selenium when heated with the solution of the electrolyte.   H. W.

Bibliography of Helium Literature.   E. R. WEAVER (*J. Ind. Eng. Chem.*, 1919, **11**, 682—688).—A bibliography of the literature connected with helium is given, including everything of scientific interest up to January, 1919. It is classified under the following headings: Discovery and Identification; Occurrence of Helium; Formation of Helium; Separation and Purification; Properties; Liquefaction and Properties of Liquid Helium; Applications of Helium; and Miscellaneous.   C. A. M.

The Stability of the Sulphones formed by the Iodides of Sodium, Rubidium, and Cæsium.   R. DE FORCRAND and F. TABOURY (*Compt. rend.*, 1919, **169**, 162—165).—The authors have measured the dissociation pressures of the sulphones formed by sodium iodide, rubidium iodide, and cæsium iodide respectively (compare this vol., ii, 341) over a temperature range from −22·5° to 20·9°. The three curves practically meet at −23°, and at the higher temperatures spread out, the sulphone of sodium iodide having the highest dissociation pressure, that of rubidium iodide the next, that of cæsium iodide being the lowest. At 760 mm., the dissociation temperatures increase with the molecular weight of the sulphone. Calculations of their heats of formation show that these vary in the inverse order.   W. G.

The **Double Magnesium Potassium Chromate Hexa-hydrate.** A. DUFFOUR (*Compt. rend.*, 1919, 169, 73—76).—The hexahydrate of the double magnesium potassium chromate, $K_2Mg(CrO_4)_2,6H_2O$, may be obtained if the two chromates are dissolved separately in equimolecular proportions in two and a-half times their weight of warm water, and the solutions are mixed, filtered, and left to evaporate at a temperature not exceeding 15°. After several days, the hexahydrate separates in tabular crystals, which should be removed at once. The crystals may be dried and analysed, but after five or six hours they begin to change slowly into the dihydrate. This dehydration is far more rapid at 120°, but always stops at the dihydrate. The hexahydrate is thus only metastable at even 10°. The crystals are monoclinic $[a:b:c = 0.7521:1:0.4984; \beta=103°54']$. This chromate shows a close analogy to the corresponding sulphate and selenate, and with its rubidium and cæsium analogues forms an eutropic triad.   W. G.

Colloidal Cuprous Oxide. RUOSS (*Zeitsch. anal. Chem.*, 1919, 58, 193—194).—One c.c. of Fehling's solution (copper sulphate 3·5 grams, glycerol 15 c.c., and sodium hydroxide 10 grams per 100 c.c.), 0·5 c.c. of 1% dextrose solution, 1·5 c.c. of urine, and 7 c.c. of water are boiled together and then filtered. The filtrate contains bright red, colloidal cuprous oxide. If 1·5 grams of potassium thiocyanate are added to the 100 c.c. of Fehling's solution, a reagent for the estimation of sugar in urine is obtained.
W. P. S.

Adsorption by Colloidal Copper Sulphide. K. SCHERINGA (*Pharm. Weekblad*, 1918, 55, 431—435).—A study of the simultaneous precipitation of zinc with the copper sulphide in the separation of copper and zinc. The amount of zinc carried down decreases rapidly with increase in the concentration of acid present and also with rise in temperature for a given acid concentration. The author concludes that the zinc is not adsorbed superficially by the copper sulphide gel, but that at the moment of precipitation a solid solution of zinc in copper sulphide is formed.   W. S. M.

The Chemistry of Burgundy Mixtures. ROBERT LUDWIG MOND and CHRISTIAN HEBERLEIN (T., 1919, 115, 908—922).

Behaviour of Hydrogen towards Iridium. A. GUTBIER, BERTA OTTENSTEIN, and G. L. WEISE (*Ber.*, 1919, 52, [*B*], 1366—1368).—The experiments were performed in the same manner as with palladium (Gutbier, Gebhardt, and Ottenstein, A., 1913, ii, 608). The occluded hydrogen is readily expelled by a slight rise in temperature, but removal of the last traces can only be effected by strong heating. The quantity of occluded gas is much smaller than with palladium. The absorption of hydrogen by

iridium with decreasing temperature is at a minimum at about 0°, and with rising temperature is at a maximum at about +20°.

H. W.

Behaviour of Hydrogen towards Platinum. A. GUTBIER and O. MAISCH (*Ber.*, 1919, **52**, [*B*], 1368—1374. Compare preceding abstract).—The occlusion of hydrogen by platinum black and spongy platinum has been investigated. The former is prepared by adding a boiling solution of chloroplatinic acid neutralised with sodium carbonate to a boiling solution of sodium formate, and is purified by washing with hot water; after being dried in a vacuum over phosphoric oxide or concentrated sulphuric acid, it retains about 0·45% of water and 0·55% of oxygen. Platinum black is converted by dilute hydrochloric acid, and frequently by prolonged boiling of suspensions of it in neutral liquids, into a greyish-black modification, which is reconverted into the black variety by treatment with sodium formate in slightly alkaline solution, or, preferably, with hydrazine hydrate solution. The greyish-black modification appears to represent an intermediate stage between platinum black and spongy platinum.

The following are the chief results of the investigation. Platinum black is far more active towards hydrogen than is spongy platinum; with the latter, the absorption of more than one volume of hydrogen was not observed, whilst with the former as much as 160 volumes were absorbed. The behaviour of platinum black with respect to absorption of hydrogen with increasing temperature is the reverse of that of spongy platinum, with which the amount of gas absorbed increases with rise of temperature. Below 0°, the absorptive capacity of both modifications of platinum diminishes. Platinum black absorbs the maximum quantity of hydrogen at 0°. H. W.

Mineralogical Chemistry.

Ferriferous Sands in Italy. U. CATTANEO and L. MADDALENA (*Ann. chim. applicata*, 1919, **11**, 99—108).—Results are given of analyses of ferriferous sands from various parts of the Latium coast, and also of the magnetites separated from such sands. The percentage of Fe_3O_4 in the sand varies from 10·22 to 13·87, and that of TiO_3 from 1·41 to 1·94. The total amount of magnetite present in these sands and others of the Italian coast is calculated to be more than 600,000 tons, 500,000 tons being contained in sand containing more than 5% of magnetite. T. H. P.

Stalactitic Barytes from Madoc, Ontario. T. L. WALKER (*Amer. Min.*, 1919, **4**, 79—80).—Curious tubular aggregates of minute, white crystals of barytes occur in veins with fluorspar and

calcite. D 4·29. Analysis shows an unusually large amount of strontium. The peculiar form of the mineral is possibly due to deposition on root fibres.

BaO.	SrO.	CaO.	MgO.	Al₂O₃.	Fe₂O₃.	SO₃.	H₂O.	Total.
43·78	13·95	0·98	1·01	1·92	0·48	36·94	0·26	99·32

L. J. S.

Canadian Minerals [Thaumasite, Saponite, etc.]. R. P. D. GRAHAM (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, IV, 191—201). —Thaumasite occurs as a soft, white coating on joint-planes at the contact of nepheline-syenite and crystalline limestone at Montreal. It forms finely fibrous or loose, mealy aggregates of minute needles. Analysis I agrees with the established formula $3CaO,SiO_2,SO_3,CO_2,15H_2O$; D 1·878. Saponite also occurs at the same locality as a soft, plastic material with much the consistency and appearance of candle grease. On exposure to air, it becomes white and opaque, finally falling to powder, which is soapy to the touch and makes a paste with water. Anal. II, of air-dried material, shows less alumina than is usual in this mineral, and agrees with Clarke's formula, $H_4(MgOH)_2Si_2O_7$. At 40° there is a loss of 8·5%, and since two-thirds of the water is given off below 100°, the formula may be written as an orthodisilicate,

$$H_2Mg_9Si_2O_7,2H_2O.$$
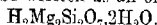
	SiO₂.	SO₃.	CO₂	Al₂O₃.	Fe₂O₃.	FeO.
I.	9·38	13·07	6·71	—	—	—
II.	46·45	—	—	3·32	0·42	0·72

	CaO.	MgO.	H₂O <100°	H₂O >100°.	Total.
I.	27·32	—	43·69		100·17
II.	—	25·91	14·48	8·13	99·43

Descriptions are also given of phenakite and of a pseudomorph of bismuthinite after molybdenite from pegmatite and quartz veins in granite at Preissac township, northern Quebec, and of albite with new crystal-forms from Ascot mine, Sherbrooke Co., Quebec.

L. J. S.

Manganotantalite from Amelia, Virginia. O. IVAN LEE and EDGAR T. WHERRY (*Amer. Min.*, 1919, **4**, 80—83).—Crystals of "columbite" occurring in albite at this locality are reddish-brown to black in colour, but in thin splinters ruby-red to orange-brown, and the streak is reddish-brown. D 6·50. H 6—6½. Compared with other members of the columbite-tantalite group, it is seen that there is a slight decrease in the a-axis with increasing tantalum content:

	Ta₂O₅. Per cent.	MnO. Per cent.	$a : b : c$.
Standish, Maine.........	9	4	0·4023 : 1 : 0·3580
Haddam, Conn..........	30	5	0·4020 : 1 : 0·3529
Amelia, Va.	53	8	0·4017 : 1 : 0·3562
Sanarka, Russia	80	14	0·4014 : 1 : 0·3505

L. J. S.

Analytical Chemistry.

Device for Guarding against Over-titration. O. HACKL (*Zeitsch. anal. Chem.*, 1919, **58**, 194—198).—A 25 c.c. pipette having practically no stem below its cylindrical bulb and having a length of rubber tubing on its upper stem is placed in the solution to be titrated. The pipette is filled, the tubing closed with a pinchcock, and the titration proceeded with until the solution is slightly over-titrated; the contents of the pipette are then allowed to flow back into the main portion of the solution, and the titration is continued cautiously until the end-point is reached. W. P. S.

The Estimation of Hydrogen Peroxide and the Conservation of Hydrogen Peroxide Solutions. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 949—959).—Hydrogen peroxide solutions may be conveniently estimated iodometrically. The titration may be carried out directly after the addition of acid and potassium iodide if a few drops of N-ammonium molybdate solution are added as a catalyst. For the conservation of peroxide solutions, the addition of 75—100 mg. of acetanilide, benzoic acid, or salicylic acid per litre is recommended. The solution should also react acid to dimethyl-yellow, and should be stored in brown glass bottles.
W. S. M.

The Titration of Iodides by means of Conductivity Measurements. I. M. KOLTHOFF (*Chem. Weekblad*, 1919, **16**, 926—929).—Iodide is completely oxidised to iodine by means of iodate in acid solution according to the equation $5I' + IO_3' + 6H' = 3H_2O + 3I_2$. If the iodide–iodate mixture is titrated with hydrochloric acid and the conductivity measured after each addition of the acid. an approximately constant value is obtained until the oxidation is complete, when a rapid increase in conductivity is observed. The end-point is sharply shown graphically by plotting conductivity against volume of acid added. Iodide may be accurately titrated in this way even in presence of a large excess of bromide, as the analogous oxidation of bromide requires a greater acid concentration and higher temperature. W. S. M.

Precipitation and Filtration of Barium Sulphate in Water Analysis. VICTOR FROBOESE (*Chem. Zeit.*, 1919, **43**, 367).—The water is rendered slightly acid with hydrochloric acid, boiled, and treated with a very small excess of barium chloride solution; when cold, the liquid is poured through a filter, the precipitate washed by decantation, and then collected on the filter. W. P. S.

Picramic Acid as a Standard in Colorimetric Estimation of Nitrogen by Nessler's Method. G. EGERER and F. FORD (*J. Lab. and Clin. Med.*, 1919, **4**, 439—442; from *Physiol. Abstr.*, 1919, **4**, 167).—The colour of picramic acid solution is practically

permanent, and the solution serves as a trustworthy standard in the estimation of ammonia by Nessler's method. W. P. S.

A Simplified Macro-Kjeldahl Method for Urine. OTTO FOLIN and L. E. WRIGHT (*J. Biol. Chem.*, 1919, **38**, 461—464). —A method by which an estimation of nitrogen in urine may be carried through in twenty to twenty-five minutes. The urine (5 c.c.) is boiled over a micro-burner with 5 c.c. of a mixture of sulphuric and phosphoric acids containing copper sulphate and 2 c.c. of 10% ferric chloride solution. Oxidation should be complete in about eight minutes, whilst the distillation may be carried through in five. Urines containing much sugar require oxidation with fuming sulphuric acid. J. C. D.

Estimation of Ammonia in Blood. SERGIUS MORGULIS and H. M. JAHR (*J. Biol. Chem.*, 1919, **38**, 435—438).—The aeration method for determining ammonia in blood is open to many inaccuracies. The authors propose to remove protein from the blood before carrying out the estimation. This they do by means of metaphosphoric acid. Ammonia in the protein-free filtrate is adsorbed by permutite, from which it is again liberated by sodium hydroxide and determined colorimetrically by the Nessler process. J. C. D.

Method for the Estimation of Nitrates in Water by means of the Phenolsulphonic Acid Reaction. ROBERT C. FREDERICK (*Analyst*, 1919, **44**, 281—284).—The presence of large quantities of chlorides (up to 100 parts of chlorine per 100,000 parts of water) does not interfere with the estimation of nitrates by the phenolsulphonic acid method if the water (25 c.c.) is evaporated with 2 c.c. of reagent containing 4 grams of phenol and 400 c.c. of sulphuric acid per litre. The evaporation should be carried as far as possible on a water-bath, the residue then dissolved in water, again evaporated, dissolved in 95 c.c. of water, the solution treated with 3 c.c. of concentrated ammonia, diluted to 100 c.c., and the coloration obtained compared with that produced by a known amount of nitrate under similar conditions. W. P. S.

Estimation of Carbon in Soils by the Wet Combustion Method. D. D. WAYNICK (*J. Ind. Eng. Chem.*, 1919, **11**, 634—637).—In estimating carbon in soils and the like by Ames and Gaither's method of wet combustion (*J. Ind. Eng. Chem.*, 1915, **7**, 561), Gortner weighed the carbon dioxide after absorption in potassium hydroxide, whilst Schollenberger (A., 1916, ii, 395) used barium hydroxide as an absorbent and titrated the excess of alkali with acid. The drawback to the first method is the time required for the absorption, and to the second the difficulty of preventing the barium hydroxide absorbing carbon dioxide from the air. These drawbacks are obviated in a simple modification of the method, in which the carbon dioxide is absorbed in a soda-lime absorption bulb and estimated gravimetrically. A

complete estimation may be made in twenty-five minutes. [See also *J. Soc. Chem. Ind.*, 1919, 591A.]   C. A. M.

Estimation of Carbon Disulphide. A Critical Examina-tion of the various Methods usually Employed. PERCY E. SPIELMANN and F. BUTLER JONES (*J. Soc. Chem. Ind.*, 1919, 38, 185—187T).—Determination of the specific gravity of benzene before and after extraction of carbon disulphide with alcoholic potassium hydroxide solution gives a fairly accurate measure of the quantity of carbon disulphide present, the error being within 0·03%. Oxidation of the above alkaline extract with bromine and estimation of the resulting sulphate are also trustworthy. Volu-metric or gravimetric estimation of the xanthate in the alkaline extract, by titration or precipitation with copper sulphate solution, was found to be untrustworthy, as was also a method depending on the precipitation of carbon disulphide with phenylhydrazine. Pre-cipitation of the xanthate with lead acetate did not yield good results.   W. P. S.

Electrolytic Separation of Lead from Chromium and Analysis of Chrome Yellow and Similar Pigments. JAROSLAV MILBAUER and IVAN ŠETLÍK (*J. pr. Chem.*, 1919, [ii], 99, 85—92).—According to Vortmann (A., 1907, ii, 302), the electrolytic separation of lead peroxide in presence of sulphuric, selenic, or chromic acid leads to high results, it being necessary to redissolve the peroxide and repeat the separation. Smith ("Electrochemical Analysis," 3rd ed., 1907, 165), however, states that lead may be separated accurately as peroxide from the alkali and alkaline earth elements, glucinum, magnesium, mercury, and aluminium, and that the presence of chromic acid is without influence on the quantitative separation. The authors find that Pb¨ may be easily separated electrolytically from Cr¨¨ if 150 c.c. of the electrolytic solution contains 0·2 gram of lead, 0·1 gram of chromium, and 20 c.c. of nitric acid (D 1·4), and that addition of 15 c.c. of per-chloric acid (D 1·12) does not invalidate the results. This method is applicable to the analysis of pigments with a basis of lead chromate, the pigment being dissolved in nitric and per-chloric acids and the diluted solution electrolysed; the chromium is afterwards precipitated as hydroxide and weighed as Cr_2O_3. [See also *J. Soc. Chem. Ind.*, 1919, September.)   T. H. P.

Estimation of Minute Amounts of Lead in Urine, Fæces, and Tissues. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1919, 38, 449—452).—The evaporated urine (2000 c.c.) or the dried tissue or fæces (500 grams) is oxidised with sodium nitrate in a silica vessel. After the oxidation, the vessel is cooled and the contents treated with 10% hydrochloric acid until the reaction is faintly acid. The mixture is heated to boiling, filtered while hot, and made faintly alkaline with ammonium hydroxide. Two or three drops of a 1% solution of copper sulphate are then added, and

the copper and any lead precipitated by the addition of hydrogen or ammonium sulphide. The suspension of sulphides is separated by centrifugalisation, and washed very carefully in order to remove magnesium, phosphates, and chlorides.

The final residue of sulphides is transferred to a platinum crucible of 25 c.c. capacity by means of 3 c.c. of dilute nitric acid (20 parts of concentrated acid, D 1·42, and 80 parts of water), and the centrifuge tube washed out with 3 c.c. of distilled water. The solution is then electrolysed with a current of 3 to 3·5 amperes and ; to 6 volts, the crucible serving as anode and a spiral of platinum wire as cathode. Within fifteen minutes, all the lead is deposited on the crucible anode in the form of a brown film of lead peroxide, whilst the copper and any traces of iron are deposited on the cathode. Care must be taken not to cut off the current while the lead peroxide is in contact with nitric acid, so that it is necessary to remove the acid by siphon while the electrolysis is proceeding, replacing it at the same time by distilled water. The crucible is washed, and 5 c.c. of a 5% solution of potassium iodide (free from iodate) and 1 c.c. of 25% acetic acid are added. The lead peroxide decomposes, giving a yellow deposit of lead iodide on the crucible and a solution of free iodine. After five minutes, the liquid is transferred to a small beaker and titrated with 0·005N-sodium thiosulphate solution.　　　　　　　　　　　　　　　　J. C. D.

Apparatus for Measuring the Volume of Gas Evolved during a Chemical Reaction. P. NICOLARDOT and M. H. ROBERT (*Chim. et Ind.*, 1919, **2**, 641—646).—A modification of an apparatus described previously by one of the authors (A., 1912, i, 597), particularly designed for measuring the volume of hydrogen liberated when aluminium is dissolved in sodium hydroxide solution. The reaction vessel consists of a tube which is connected with a reflux apparatus, and this in turn with the measuring burette. The latter is filled with water and is surrounded by a water-jacket. A diagram of the apparatus is given in the original and the method of using it is explained in detail.　　W. P. S.

Estimation of Iron in Iron Ores by means of Permanganate. L. BRANDT (*Chem. Zeit.*, 1919, **43**, 373—374).—The use of colloidal silica as recommended by Schwarz and Rolfes (this vol., ii, 170) to prevent the action of hydrochloric acid on permanganate in the titration of ferrous salts is untrustworthy. It is shown that the larger the quantity of silica added, the less permanganate is required for the titration. This occurs in both hydrochloric and sulphuric acid solutions.　　W. P. S.

Rapid Method for Estimating Nickel and Cobalt in Ores and Alloys. III. W. R. SCHOELLER and A. R. POWELL (*Analyst*, 1919, **44**, 275—280. Compare A., 1917, ii, 425).—Further work on the method described previously showed that modification is necessary when the material contains manganese or certain other

elements; the addition of solid potassium iodide instead of saturated sodium chloride solution to the ammoniacal tartrate solution promotes complete precipitation of the cobalt as hexaminecobaltous iodide in the case of ores containing little or no nickel. The following is a summary of the procedure recommended for the analysis of ores.

(1) The ore is free from copper, manganese, calcium, and magnesium; presence of arsenic immaterial. The sample is dissolved in nitric acid, the solution evaporated almost to dryness, and tartaric acid (ten times the weight of tervalent metals present) dissolved in water is added. The mixture is then treated with 50 c.c. of concentrated ammonia and 3 to 5 grams of potassium iodide, and, after fifteen minutes, the precipitate is collected, washed with ammoniacal potassium iodide solution, and dissolved in dilute hydrochloric acid. The solution is filtered, the cobalt precipitated as phosphate, and the nickel titrated in the filtrate from the latter precipitate.

(2) The ore contains copper, otherwise the same as (1). The method is the same as that above up to the point where the iodide precipitate is dissolved in hydrochloric acid. The solution is decolorised by the addition of sulphurous acid, boiled, cooled, filtered to separate cuprous iodide, etc., and the cobalt then precipitated as phosphate.

(3) General procedure for ores free from manganese. The acid solution of the ore is treated with hydrogen sulphide, filtered, the filtrate treated with ammonium chloride and a slight excess of ammonia, and saturated with hydrogen sulphide. The precipitate obtained is dissolved in aqua regia, and the solution is evaporated almost to dryness, etc., as described under (1).

(4) The ore contains manganese. If only small amounts of manganese are present, the ammonium cobalt phosphate precipitate may be titrated with $N/5$-acid (not hydrochloric acid), or the, weighed cobalt pyrophosphate precipitate may be dissolved in sulphuric acid and the amount of manganese estimated by the persulphate–silver nitrate method. For large amounts of manganese, the mixed iodide precipitate is dissolved in dilute acid, and the nickel and cobalt precipitated as sulphides from an acetic acid solution, or the acid solution may be neutralised and the cobalt and nickel precipitated as xanthates. In the case of nickel ores free from cobalt, manganese does not interfere with the cyanide titration in the presence of citrate.   W. P. S.

Estimation of Urea. PHILIBERT (*J., Pharm. Chim.*, 1919, [vii], **19**, 335—346. 386—397, 434—441).—A method which is more trustworthy than those described by Folin and by Fosse (A., 1917. ii. 73), particularly in the case of urine containing sugar, consists in treating 10 c.c. of the urine with 2 c.c. of basic lead acetate solution, diluting the mixture to 50 c.c., and filtering. Ten c.c. of the filtrate are treated with 5 c.c. of 10% sodium hydroxide solution in the ureometer, a definite volume of hypobromite is

added, and the mixture shaken so as to mix it thoroughly with the mercury contained in the apparatus. The gas evolved is measured under the usual conditions. A control experiment is made, using a standard urea solution and the same quantities of reagents as in the first experiment. Allowance is made for any ammonia present, this being estimated separately. W. P. S.

Ureometer with a Reaction Bulb of Variable Capacity. BOYER (*J. Pharm. Chim.*, 1919, [vii], **19**, 346—349).—The apparatus consists of a wide tube constricted at its lower end so as to form a graduated tube; the wide tube is divided into two parts, which are connected by a rubber tube which keeps the two ends a short distance apart. Hypobromite solution and water are introduced into the apparatus so as to fill the graduated portion, a glass ball is then placed in the apparatus, thus closing the top of the graduated tube, and the solution in which the urea is to be estimated is added. The two wide tubes are now pressed together, thus folding the rubber connexion in pleats, the whole apparatus is filled with water, closed with a rubber stopper, and inverted. The contents mix, the volume of the gas liberated being accommodated by the rubber connexion; the total volume of the gas is determined in the usual way. W. P. S.

A Reaction for Lecithin. H. J. HAMBURGER (*Arch. Néerland. physiol.*, 1919, **3**, 361—364).—This test will detect 0·01% of lecithin present in fluids containing proteins. The proteins are removed by adding three volumes of 96% alcohol and filtering or centrifugalising. On the addition of dilute sulphuric acid (1:5) to the clear filtrate, a cloudy precipitate of lecithin is formed, which dissolves on warming and reappears on cooling. J. C. D.

Detection and Estimation of Cocaine, Heroine, and Veronal in Viscera. P. A. ELLIS RICHARDS (*Analyst*, 1919, **44**, 192—196).—A weighed portion of the viscera is acidified with acetic acid and extracted with warm alcohol; the alcoholic solution is concentrated, filtered, clarified with lead acetate, and the excess of lead removed as sulphide, again concentrated, acidified with acetic acid, and extracted with ether. The ethereal extract is evaporated, the residue dried, weighed, and examined for veronal, trional, sulphonal, etc. The aqueous solution, after the extraction with ether, is rendered ammoniacal, extracted with chloroform, the chloroform solution shaken with dilute hydrochloric acid, this acid extract again rendered ammoniacal, extracted with chloroform, and the residue, if any, obtained after evaporating the chloroform, is extracted with benzene, in which cocaine is distinctly soluble. For the examination of the urine, the sample is acidified with acetic acid, boiled, clarified with lead acetate, and then treated as in the case of viscera. The final residues are then submitted to special tests for their identification.

Notes are given on tests for certain narcotics. [See, further, *J. Soc. Chem. Ind.*, 1919, 512A.]   W. P. S.

The Metabolism of Bile Acids. I. A Quantitative Method for Analysis of Bile Acids in Dog's Bile. (Miss) M. G. FOSTER and C. W. HOOPER (*J. Biol. Chem.*, 1919, **38**, 355—366). —Dog's bile contains taurocholic and taurocholeic acids, which, on hydrolysis, yield cholic and choleic acids and taurine. Taurine reacts quantitatively with nitrous acid under the conditions employed in the Van Slyke apparatus, and this fact is made the basis for the analytical procedure. Five c.c. of bile cleared in a centrifuge are precipitated with 40 c.c. of 96% alcohol, and heated to boiling point to ensure complete solution of the acids. After cooling, the mixture is made up to 50 c.c. with 95% alcohol and passed through a dry filter. Two portions of 20 c.c. are evaporated to dryness. One is washed out with water and made up to 10 c.c. in a volumetric flask. Samples of 2 c.c. of this are used to determine the nitrogen present in amino-form before hydrolysis. The other sample is hydrolysed by being heated on the water-bath for five hours with 6 c.c. of 8% sodium hydroxide. This sample is made up to 10 c.c. and the amino-nitrogen again determined in 2 c.c. portions. The difference represents the nitrogen present in the amino-group of taurine. For conversion of the nitrogen figure into one representing taurocholic acid, the factor 36·72 is used.
J. C. D.

An Electrical Method of Determining the Lime Requirement of Soils. C. J. LYNDE (*Trans. Roy. Soc. Canada*, 191⁻,,) [iii], **12**, III, 21—26).—Two lots of 10 grams each of soil a shaken respectively with 150 c.c. of distilled water and 150 c. of a solution of calcium hydrogen carbonate for three hours, as the Hutchinson and MacLennan method (compare A., 191⁻, ii, 784). The electrical resistance of the aqueous soil solution of the calcium hydrogen carbonate solution before and after shaking with the soil is determined. If these are represented by r_1, r_2, and OR respectively, then the value of r, the calculated resistance of the calcium hydrogen carbonate solution after being shaken with the soil and allowing for the resistance of the aqueous soil solution, is given by $r = r_1 \times OR / (r_1 - OR)$. Then the ratio r/r_2 should give a measure of the alkalinity or acidity of the soil. Comparing these results with those obtained by the Hutchinson and MacLennan method (*loc. cit.*), it is found that if the ratio is less than 0·986, the soils are alkaline, whilst if the ratio is above 1·284, the soils are acid and require liming.   W. G.